CHAPTER 6

WATER AND WASTE WATER PROBLEMS

6.1. INTRODUCTION TO THE PROBLEMS OF WATER AND WASTE WATER.

Water pollution problems were surveyed in section 5.5, and this chapter is devoted to linking these problems with the various water treatment methods available.

Selection of the optimum waste water and water treatments is a very complex problem. Quantitative management requires the application of the principles presented in Part A of this book, often in the form of an ecological model. The search for an optimum solution also requires a comprehensive knowledge of the treatment methods available. Furthermore, the problem is complicated by the interdependence of water supply and waste water disposal.



Fig. 6.1. Example of good water management practice, where 1) a part of the treated waste water is reclaimed for industries after an additional treatment, 2) The industrial waste water is treated before being discharged into the public sewage system. The sewage treatment chosen pays regards to as well the lake as the water treatment.

Good water management practice should therefore consider not only the ecological effects in the receiving body of water, but also the effect on the quality and economy of the water supply. Fig. 6.1 illustrates these considerations.

Effluents fall into seven groups, but many have, to a greater or lesser degree the polluting properties of at least two of these categories:

- 1. Organic residues, including domestic sewage, effluent from food-processing-industries, ensilage, manure heaps and cattle yards, laundries, paper mills, etc. These effluents vary a great deal, but they have much in common. They all contain complex organic compounds in solution and/or suspension, sometimes with toxic substances and various salts. Their basic property, however, is that they contain unstable compounds, which are readily oxidized and so use up the dissolved oxygen in the water. Some of these compounds are more readily decomposed than other: for example, slaughterhouse wastes oxidize rapidly while wood pulp is comparatively stable. Section 6.2 focuses on the technical solutions to this problem, while section 2.6 in Part A deals with the effects of organic residues on ecosystems.
- Nutrients, including ammonia, nitrates, other nitrogenous compounds, orthophosphates, other phosphorous compounds, silica and sulphates. The main sources are domestic sewage and effluents from fertilizer manufacture. Discharge of nutrients may cause undesirable eutrophication as described in section 2.8. Section 6.3 discusses the methods available for nutrient removal.
- 3. **Poison** in solution occur in the waste waters from many industries. They include acids, alkalis, oil, heavy metals and toxic organic compounds, mainly from chemical industries, gas works and use of insecticides. Their effects on ecosystems are described in section 2.13. 6.5 reviews the methods available for the removal of heavy metals and 6.4 deals with removal of toxic organic compounds.
- 4. Inert suspensions of finely divided matter result from many types of mining and quarrying and from washing processes, such as those of coal and root crops. The effect of these pollutants on the ecosystem can be evaluated from the principles mentioned in chapter 2. Removal of inert finely divided matter can be carried out by mechanical treatment methods mentioned in 6.2.2.
- 5. Other inorganic agents, such as salts or reducing agents (e.g. sulphides, sulphites and ferrous salts) occur as constituents of the effluent of several types of industry. Minor discharges of salts are generally harmless to the environment, but reducing compounds use up the oxygen in the receiving body of water, and have the same effect as organic residues (see 2.6). This effect can, however, easily be eliminated by aeration, a process which will only be discussed in relation to

biological treatment methods (see 6.2.3). For a more comprehensive account, see Jørgensen (1979).

- 6. Hot water is produced by many industries that use water for cooling purposes. They often use river water, which is pumped through the cooling system and sometimes raised to very high temperatures during part of its journey. The effects of this process are described in section 2.4. The methods available to meet this problem are a) use of cooling towers, b) use of heat exchangers, c) use of alternative technology, d) use of alternative receiving water body which is less susceptible to damage. These solutions will not be discussed in this context, as they either must be considered as purely industrial engineering problems, or have already been mentioned in chapters 2 and 4.
- 7. **Bacteriological contamination** of waters originates mainly from domestic sewage, but food-processing industries, manure heaps and cattle yards are also sources of this type of pollution. Methods to meet this problem are used in the production of potable water, for process water in industry and in the treatment of waste water. The available methods are mentioned in 6.6.5.

Waste waters emanate from four primary sources: 1) municipal sewage, 2) industrial waste waters, 3) agricultural runoff and 4) storm water and urban runoff. The problem of the first group is related mainly to organic residues and nutrients, while the second group encompasses the entire spectrum of pollution problems, although discharge of heavy metals and organic compounds are the most serious ones. It is not possible to give comprehensive review on industrial waste water problems here; for detailed discussion see Jørgensen (1979).

As municipal and industrial waste waters receive treatment, increasing emphasis is being placed on the pollutional effects of urban and agricultural runoff. The range of pertinent characteristics of these waste waters is given in Table 6.1.

In many places sewage continues to be discharged into systems of drains intended also for the removal of surface runoff from rainstorms and melting snow or ice. This is called combined sewerage. However, in most modern developments, sewage and runoff are each colleted into a separate system of sanitary sewers and storm drains in order to avoid pollution of water course by the occaaional spillage of sewage and stormwater mixtures. This is called separate sewerage.

Often the receiving body of water also serves as an important source of supply for many purposes. It is this multiple use of natural waters that creates the most impelling reasons for sound water-quality management, as already mentioned above. This part of the problem is discussed in section 6.6.

Agricultural pollution problems are related to:

- 1. the extensive use of natural and industrially produced fertilizers to increase yield,
- 2. use of pesticides to eliminate damage by pests
- 3. waste from domestic animals.

It seems only possible to solve problems 1) and 2) by use of sound ecological engineering, which has been treated in section 4.10. Waste-water and solid-waste problems related to 3) are, in principle, not different from municipal and industrial waste problems and are therefore touched on in this part of the book.

TABLE 6.1

Pollution from urban and agricultural runoff

Constituent	Urban runoff (Storm water)	Agricultural runoff
Suspended solids (mg/l) Chemical oxygen demand	5 - 1200	
COD (mg/l) Biological oxygen demand	20 - 610	-
BoD (mg/l) Total phosphorus (mg/l) Nitrate nitrogen (mg/l) Total nitrogen (mg/l) Chlorides (mg/l)	1 - 173 0.02- 7.3 0.3 - 7.5 3 - 35	1.1- 0.65 0.03- 5.0 0.5- 6.5

TABLE 6.2 Operations

Operation	Detailed description, see	
Screening Settling	6.2.2 6.2.2	
Filtration	6.2.2	
Biological decomposition	6.2.3	
Chemical precipitation	6.2.5 6.3.2 + 6.5.2	
Nitrification	6.3.2 + 6.5.2 6.3.3	
Stripping	6.3.4 6.3.4	
lon exchange Algae ponds	6.3.6 + 6.5.3 6.3.7	
Adsorption Chemical oxidation	6.4.3 6.4.4	
Chemical reduction Extraction	6.4.4 + 6.5.2 6.5.4	
Membrane processes	6.5.5	

Almost all unit operations applied for water and waste water treatment

are mentioned in this chapter. Some of the individual operations can, however, be used to solve more than one pollution problem. The general description of these operations are given in context with their area of major application, and can be found in accordance with Table 6.2.

6.2. REDUCTION OF THE BIOLOGICAL OXYGEN DEMAND.

6.2.1 The BOD_s -problem and its sources.

When organic matter is added to an aquatic ecosystem it is immediately attacked by bacteria, which break it down to simpler substances, using up oxygen in the process, see section 2.6. The rate of which a particular type of effluent is able, in the presence of ample oxygen, to satisfy its oxygen demand depends on what it contains. Industrial effluents which contains only chamical reducing agents, such as ferrous salts and sulphides, take up oxygen purely by chemical reactions. They do this very rapidly, exerting what is called immediate oxygen demand. Organic substances, such as carbohydrates, proteins, etc., become oxidized by the activities of bacteria. The rate at which they are broken down therefore depends first on the presence of suitable bacteria and second on how satisfactory and balanced a food they are for microorganisms. Compounds which are more or less refractory are decomposed at a low or very low rate. They will therefore not make a significant contribution to the BOD₅.

These compounds are more or less toxic to the aquatic flora and fauna, and section 6.5 deals with methods of removing toxic organics, which obviously cannot be removed by the same methods as biodegradable organic matter.

Readily biodegradable matter has a biological oxygen demand, which can be calculated theoretically by using the reaction scheme. Waste water containing 100 mg l^{-1} of glucose will have a BOD₅ of 110 mg l^{-1} , which is in accordance with the following reaction:

$$C_6H_{12}O_6 + 6O_2 - 6CO_2 + 6H_2O$$
 (6.1)

Glucose is easily broken down to CO_2 and H_2O , oxidation being complete in less than 5 days. However, other components readily oxidized but at a lower rate will not give a BOD_5 in accordance with the reaction of decomposition because a part of their mass is synthesized into new bacterial substances, which will not be broken down during the 5-days period.

For a more complex mixture of organic compounds the decomposition

reaction might be written as follows:

$$COHN + O_2 \xrightarrow{(cells)} CO_2 + H_2O + NH_3 + cells \qquad (6.2)$$

As mentioned in 6.1 the major sources of organic residues are domestic sewage and the food industry. Table 6.3 gives the range of concentration of pertinent characteristics of domestic waste water in the case of separate sewerage.

TABLE 6.3 Concentration of pertinent characteristic of domestic waste water (mg 1⁻¹)

P _{total} 6 - 12	BOD ₅ 1 50 N _{total} 2 5 P _{total} 6	-	- 34	300 15 2
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The consumption of water in the food industry is shown in Table 6.4, which demonstrates that the food industry makes a significant contribution to the overall pollution problem due to its high water consumption and relatively high BOD_5 .

The composition of domestic sewage varies surprisingly little from place to place, although, to a certain extent, it reflects the economic status of the society. A typical organic composition of domestic waste water is given in Table 6.5. A more detailed analysis reveals that domestic sewage is a very well balanced food for microorganisms. It contains sufficient amounts of essential amino acids, nutrients and vitamins. Consequently its biological decomposition causes few problems; most difficulties with biological treatment plants are related to the discharge of more or less uncontrolled amounts of industrial waste water (see also 6.4.1 and 6.5.1).

TABLE 6.4

Pollution from the food-processing industry in Denmark (Denmark is a country with a highly developed food industry)

Branch	Production tons/year (round figures)		Million m ³ waste water/year	BOD ₅	10 ⁵ ⁺) person equivalents	
Abattoirs	600,000	20	12	1500	8.0	
Dairies	5,000,000	1.5	7.5	1800	6.0	
Fish filletting plants	100,000	2	0.2	5500	0.5	
Potato starch production	25,000	30	0.75	5500	1.9	
Breweries	600,000	10	6	1500	4.0	

*) 60 g BOD₅/24h per inhabitant

Organic		Concentration	=
constituent	Soluble	Particulate	Total
	(mg/l)	(mg/l)	(mg/l)
Total Carbohydrate	30.5	13.5	44.0
Free Amino Acids	3.5	0	3.5
Bound Amino Acids	7	21.25	28.25
Higher Fatty Acids	0	72.5	72.5
Soluble Acids	22.75	5	27.75
Esters	0	32.7	32.7
Anionic Surfactants	11.5	4	15.5
Amino Sugars	0	0.7	0.7
Amide	0	1.35	1.35
Creatinine	3.1	0	3.1
Fraction sum	78.35	151	229.35
Present in Waste Water	94	211.5	305.5

TABLE 6.5Organic composition of domestic waste water

Reduction of BOD_5 in domestic waste water and other types of waste with a similar composition is carried out by a combination of mechanical and biological treatment methods.

P.6.1. Mechanical methods remove suspended matter in one or more steps, with the aim of not only removing the coarser inorganic pariticles, but also reducing the BOD₅ in accordance with the amount of suspended organic matter.

In principle, the entire BOD_5 -reduction could be carried out using biological treatment methods alone, but this will often prove more expensive, than a combined mechanical and biological treatment. The results of the combined treatment are outlined in 6.2.4.

6.2.2 Mechanical treatment methods.

P.6.2. Mechanical treatment methods comprise screening, sand trap, sedimentation, filtration and flotation.

Screening. Screens are used for removing larger particles, such as branches, rage, etc. They are made from iron bars or gratings and can be classified according to the distance between the bars as coarse (40-100 mm) and fine (10-40 mm). Screens need to be cleaned frequently, either manually or mechanically by rakes. The purpose of the screens is to protect pumps and other mechanical equipment. The removed material is either

composting or by incineration.

Sand traps. The sand trap or grit chamber removes mainly inorganic particles 0.1-3 mm in size. It operates by sedimentation, but due to a short retention time (10-20 minutes) and air stirring, the finer organic particles are prevented from settling. Fig. 6.2 shows a sand trap at a municipal sewage plant.



Fig. 6.2. A sand trap at a municipal sewage plant.

Sedimentation. Sedimentation is used to remove suspended solids from waste water. In principle, it is the same process as is used in nature, see section 2.6.

A settling tank has three main functions:

- 1. It must provide for effective removal of suspended solids so that its effluent is clear.
- 2. It must collect and discharge the subnatant stream of sludge.
- 3. It must thicken the sludge to a certain concentration of solid.

Three distinct types of sedimentation may be considered:

1. Discrete settling. This is the settling of a dilute suspension of particles which have little or no tendency to flocculate.

- 2. Flocculent settling, which occurs when the settling velocity of the particles increases as they fall to the bottom of the tank, due to coalescence with other particles.
- 3. Zone settling, which happens when interparticle forces are able to hold the particles in a fixed position relative to each other. In this case the particles sink as a large mass rather than as discrete particles.

Plug flow is never achieved in practice. Some of the particles will be short circuited and will therefore be held in the tank for a time less than V/Q, where V = the tank volume (m^3), and Q = the flow rate (m^3/h).

Wind effects, hydraulic disturbances and density and temperature effects will all result in a deviation from the ideal plug flow. Short circuiting in a tank can be characterized by tracer techniques. Dye, salt or radioactive materials are introduced into the inlet and the concentration distribution in the effluent stream indicates the flow patterns. Some typical curves for effluent concentration versus time are shown in Fig. 6.3.



Fig. 6.3. Effluent concentration versus time.

The relative concentration 1.0 corresponds to the concentration achieved by complete mixing, and curve A shows the results of such an experiment, where the tank content was completely mixed. Curve B is typical of a wide shallow regular tank, while curve C represents the situation in a long narrow tank. Curve D represents a baffled tank and is, as shown, close to the ideal case for plug flow E. The results of studies by Dague and Baumann (1961) are shown in Fig. 6.4. Centre and peripheral feed circular clarifiers were examined my means of dye dispersion. As can be seen, the difference between the two feeding methods is significant.



Fig. 6.4. 1) Feed in centre, 2) Feed in periphery, 3) Theoretical retention time.



sludge out

Fig. 6.5. Steeply inclined tube settler.

It is frequently possible to improve the performance in an existing settling tank by making modifications based on the results of a dispersion test. The addition of stream-deflecting baffles, inflow dividing mechanism and velocity dispersion feed wells may decrease short circuiting and increase efficiency.

Fig. 6.5 illustrates the principle of tube settlers. The design incorporates the use of very small diameter tubes in an attempt to apply the shallow depth principle as suggested by Camp (1946).

Flow through tubes with a diameter of 5-10 cm offers optimum hydraulic conditions and maximum hydraulic stability. Culp et al. (1968) have reported excellent results using tube settlers with a retention time of less than 10 minutes. The retention time can be calculated in accordance with the following equation:

$$Y_{A} = v_{s} \left(\frac{L}{S} \cos \beta + 1\right)$$

(6.3)

where

 $Y_A = \frac{Q}{A} = \frac{flow rate}{area of tube settler}$

L = length of tube

S = distance between the tubes (the diameter of the tubes)

 β = the angle of the tube to the horizontal (see Fig. 6.5)

v_s = direct settling rate

As can be seen from this equation, Q/A will increase as β decreases. It should therefore be an advantage to place the tubes as near as possible to horizontal. However, the horizontal settler is not self-cleaning and must be back-washed. Therefore, the steeply inclined 60° tube settler is more commonly used. Continuous gravity draining of settled solid might be achieved from tubes inclined of angles between 45 and 60°.

The clarifier may be designed as a rectangular or circular tank, and may utilize either centre or peripheral feed. The tank can be designed for centre sludge withdrawal or for withdrawal over the entire tank bottom. The different types of tank are shown in Figs. 6.6 and 6.7. The first one is designed for small flows, where the height of the tank is only moderate in spite of the angle of the cone.

The second clarifier is made of concrete and is able to deal with a considerably larger flow rate. An inlet device is designed to distribute the flow across the width and the depth of the settling tank, and correspondingly an outlet device is designed to collect the effluent uniformly at the outlet end of the tank.

It is very difficult to design a full-scale sedimentation tank based on settling experiments, as several important factors influencing particle behaviour in a full-scale operation are neglected in such experiments. Tanks are subject to eddies, currents, wind action, resuspension of sludge, etc. A full-scale clarifer will therefore show a slightly reduced efficiency compared to settling experiments, but this can be taken into consideration by incorporating a safety factor. The choice of an acceptable safety factor requires experience. The practical factor might vary form 1.5 when the tank is very small, baffled and protected form wind, to 3.0 in the case of a large tank, unbaffled and unprotected from wind. Even with the use of the safety factor, however, perfect performance should not be expected.



Fig. 6.6. Settling tank for small flow rattes.



Filtration. Water treatment by filtration uses principally either deep granular filters or precoat filters.

Deep granular filters are either silica sand or a dual medium or multi-media filters. A dual medium filter of coal over sand is widely used, and multi-media filters consisting, for example, of coal over silica sand over garnet sand, are finding increasing application. Precoat filters use diatomaceous earth, perlite or powdered activated carbon.

Sand filters were developed in England in the middle of the 19th century. These filters operated at a relatively low rate, between 0.1 and 0.3 m/h. Today the same filters are used at rates of up to 0.6 m/h, and are known as slow sand filters in contrast with the rapid sand filters developed later in the 19th century in the U.S.A., which operate with a filtration velocity of 3 to 10 m/h.

The present filters, which consist of a number of porous septa in a filter housing, have found wide application since the second World War. The septa support is a thin-layer filter medium, which is deposited on the outside of the septa at the beginning of the filtration cycle.

As mentioned above, sand filters can be divided into two classes - slow

filters and rapid filters. There are two main differences between them: 1. As shown in Table 6.6, the properties of the filter media are different. The effective grain size is the diameter of the largest grain of sand in that 10% of the sample by weight which contains the smallest grains. The uniformity coefficient is the ratio of the largest grain in th 60% of the sample by weight which contains the smallest grain, to the effective size.

As can be seen rapid filters operate with a higher effective size and a smaller uniformity coefficient. The finer the sand used, the smaller will be the turbidity of the treated water and the flow rate.

TABLE 6.6Typical properties of filter media

	Slow sand filter	Rapid sand filter
Effective size (mm) Uniformity coefficient Material	0.45-0.60 1.50-1.80 sand and/or cru- shed anthracite	0.6-1.0 1.2-1.8 multi media

2. Slow filters operate for 10 to 30 days. By then the head loss will be 1 m of water or more. The filtration is interrupted and 1.5 to 4 cm of the filter sand is removed. When the sand layer reaches a height of about 40 cm, new or washed sand is added to replace up to 30 cm of the sand layer removed. In rapid filtration, impurities are removed by back-washing, usually by reversing the flow of water through the filter at a rate adequate to lift the grains of the filter medium into suspension. The deposited material thus flushed up through the expanded bed is washed out of the filter.

The rapid filter can be either an open filter or a pressure filter. Open filters are mainly built of concrete, whereas pressure filters are water-tight steel tanks which are usually cylindrical and may stand either horizontally or vertically. The most common use of pressure filters is in small cities treating ground water supplies for iron and manganese removal, in swimming pool filtration or for polishing industrial water.

The filtration cycle by use of precoat filtration consists of three steps:

- 1. Precoating
- 2. Filtration
- 3. Removal of the spent filter cake

A precoat thickness of 1.3-3 mm is generally used. During filtration the suspended solids are removed on the precoat surface resulting in an increasing pressure drop across the filter. Due to the hydraulic compression of the solid, the filtration cycle may be very short unless additional filter aid is used during filtration. The amount required varies with the type and concentration of suspended solids in the treated water. A typical pressure



Fig. 6.8. Head loss plotted against volume for a precoat filter. Filtration should be interrupted at (1).

Flotation. Flotation is used to remove suspended solid from waste water and to concentrate sludge. Thus flotation offers an alternative to sedimentation, especially when the waste water contains fat and oils.



Fig. 6.9. Flotation unit. Either a portion of the waste water or the clarified effluent is

pressurized at 3-6 atm. When the pressurized water is returned to normal atmospheric pressure in a flotation unit air bubbles are created. The air bubbles attach themselves to particles and the air-solute mixture rises to the surface, where it can be skimmed off, while the clarified liquid is removed form the bottom of the flotation tank.

Fig. 6.9 shows a flotation system with partial recirculation of the effluent. Generally it is necessary to estimate the flotation characteristics of the waste water by use of a laboratory flotation cell:

- 1. The rise of the sludge interface must be measured as a function of time. An example is shown in Fig. 6.10.
- 2. The retention time must be varied and the corresponding saturation of pressurized water determined, see Fig. 6.11.
- 3. The effluent quality must be determined as a function of the air/solids ratio, see Fig. 6.12.

Based on such results it is possible to scale up.



Fig. 6.10. Rise characteristics of paper fibres at four different air/solids ratios. 1) 0.03, 2) 0.06, 3) 0.16 and 4) 0.30.



Fig. 6.11. Saturation plotted to retention time. (Paper fibres, pressure = 9 atm.). Retention time is indicated in minutes.



Fig. 6.12. Effluent quality versus air/solids ratio. Results of laboratory experiments on 550 mg/l waste water from a paper machine.

6.2.3 Biological treatment processes.

P.6.3. Many types of biological processes are active in the breakdown of organic matter.

A nutritional classification of organisms is given in Table 6.7.

TABLE 6.7 Nutritional classification of organisms

Class	Nutritional requirements
Autotrophic	The organisms depend entirely on inorganic compounds
Heterotrophic	Organic compounds are required as nutrient
Phototrophic	Use radiant energy for growth
Chemotrophic	Use dark redox reaction as energy source
Lithotrophic	Use inorganic electron donors (e.g. hydrogen gas, ammonium ions, hydrogen sulphate and sulphur)
Organotrophic	Require organic compounds as electron donors
Strictly aerobic	Cannot grow without molecular oxygen, which is used as oxidant
Strictly anaerobic	Use compounds other than oxygen for chemical oxidation. Sensitive to the presence of minor traces of molecular oxygen
Facultative anaerobic	Can grow either in the presence or absence of air.

P.6.4. Most biological systems used to treat organic waste depend upon heterotrophic organisms, which use organic carbon as their energy source.

As seen in the table, the organisms can be either strictly aerobic, strictly anaerobic or facultative anaerobic. Anaerobic breakdown is used in the treatment of sludge, or denitrification where nitrate is the oxygen source. Chemolithotrophic organisms are also used in biological treatment processes. These comprise specialized groups of bacteria which are able to oxidize inorganic compounds such as those of hydrogen, sulphur or ammonia.

P.6.5. Of the various types of metabolism in which the redox reaction provides the ultimate source of energy, there are three major classes of energy-yielding processes:

Fermentation, in which organic compounds serve as the final electron acceptors;

Respiration (aerobic), in which molecular oxygen is the ultimate electron acceptor;

Respiration (anaerobic), in which inorganic compounds - not oxygen - are ultimate electron acceptors.

These reactions can be described by the following overall process:

Organic matter +
$$O_2$$
 + NH_2 + cells + CO_2 + H_2O + new cells (6.4)

Nitrification results from a two-step oxidation process. First, ammonia is oxidized to nitrite by Nitrosomonas. Second nitrite is oxidized to nitrate by Nitrobacter:

$$2NH_4^+ + 3O_2 + 2NO_2^- + 2H_2O + 4H^+$$
 (6.5)

$$2NO_2 + O_2 + 2NO_3$$
 (6.6)

Respiration and nitrification are the same processes as those used in nature to oxidize organic matter and ammonia. The processes are of importance for the oxygen balance of streams, as presented in section 2.6.

Nitrate can be used as an oxygen source for the biological decomposition of organic matter. The reaction - called denitrification - is:

$$2NO_2 + H_2O \neq N_2 + 2OH + 5O$$
 (6.7)

In comparison with molecular oxygen supplied by the aeration method, the use of nitrate as an oxygen source is undoubtedly easier because of its extremely high solubility. Further, it can be expected that satisfactory biodegradation of organic matter may be carried out with microorganisms and waste water containing nitrate. Industrial waste water, especially from petrochemical plants, sometimes contains a large amount of nitrate as well as highly concentrated organic matter. The application of a biological treatment method for treating such waste water using nitrate as the oxygen source is therefore attractive.

Studies by Miyaja et al. (1975) have shown that the amount of BOD_5 removed by biological treatment with nitrate as an oxygen source is linearly related to the amount of nitrate removed in the reaction tank. Studies have shown that one of the microorganism involved is Pseudomonas denitrificans.

P.6.6. Cellular growth can often be described as a first-order reaction:

$$\frac{\mathrm{dX}}{\mathrm{dt}} = \mu_{\mathrm{m}} + \mathrm{X} \tag{6.8}$$

where

X = concentration of volatile biological solid matter

 μ_m = the maximum growth rate

t = time

Integration of this equation where $X = X_0$ and t = 0, gives:

$$\ln \frac{X}{X_0} = \mu_m * t \tag{6.9}$$

This equation is only valid during the so-called logarithmic growth phase in which the substrate (the organic matter) is unlimited. When the substrate becomes the limiting factor, the growth rate can be described by means of the following equation:

$$\frac{\mathrm{dX}}{\mathrm{dt}} = \mu_{\mathrm{m}} \, \mathrm{X} \, * \, \mathrm{S} \, * \, \frac{1}{\mathrm{K}} \tag{6.10}$$

where S = substrate concentration and $K_s = a$ constant.

These two expressions can be combined by means of the Michaelis-Menten equation:

$$\mu = \mu_m \frac{S}{S + K_S}$$
(6.11)

where

$$\mu$$
 = growth rate (= $\frac{dX \cdot 1}{dt \cdot X}$)

 $\mu_m =$ maximum growth rate

- S = substrate concentration
- K_e = Michaelis-Menten constant

As can be seen, when S — ∞ the equation becomes (6.8) and when K_S >> S the equation is transformed into (6.10).

Fig. 6.13 shows the Michaelis-Menten relationship; the growth rate is plotted against the substrate concentration.

It is often convenient to illustrate the Michaelis-Menten equation by means of a Lineweaver-Burk plot. The reciprocals of the growth rate and of the substrate concentration are plotted against each other (see Fig. 6.47).

The relationship is linear as can be seen from equation (6.11) which can be transformed to:

1	Ks	<u> </u>	1	
μ =	$\overline{\mu}_{m}$	[•] 5	$+ \overline{\mu}_m$	(6.12)





Equation 6.8 is incomplete without an expression to account for depletion of biomass through endogenous decay (respiration). A first-order expression could be used:

$$\frac{dX}{dt} (end) = -k_d * X$$
(6.13)

Incorporation of endogenous decay and (6.11) into (6.8) results in:

$$\frac{dX}{dt} = \mu_{m} \frac{S}{K_{s} + S} * X - k_{d} * X$$
(6.14)

By use of the yield constant, a (a = mg biomass produced per mg of substrate used), dX can be expressed in terms of substrate removal:

$$dX = -a \circ dS \tag{6.15}$$

Combining equations (6.15) and (6.11) gives:

$$\frac{-dS}{dt} = \frac{\mu_m}{a} + \frac{S}{S+K_s} + X$$
(6.16)

The set of equations (6.8) to (6.16) is not valid for complex substrate mixtures, but in many cases the equations can be used as good approximations.

Equation (6.16) is related to the first-order kinetic equation (2.35) in section 2.6. If X can be considered constant and $K_s >> S$, which is a good approximation in many water courses, (6.16) will correspont to a first-order decomposition equation: $L \sim S$ and K_1 to $\frac{\mu_m * X}{a}$

Temperature influences these processes significantly. The effect of temperature on the reaction rate can be expressed by the following relationship:

 $\mu_{T} = \mu_{20^{\circ}C} * \pi^{T-20^{\circ}C}$ (6.17)
where $\pi = a \text{ constant.}$

 π is listed in Table 6.8 for various types of processes.

Temperature	effects	on	biological	processes	
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Process	n	
Activated sludge (low loading) Activated sludge (high loading) Trickling filter Lagoons Nitrification	1.00 - 1.01 1.02 - 1.03 1.035 1.05 - 1.07 1.143	

The progress of aerobic biological purification is shown in Fig. 6.14. Note the slow BOD_5 reduction after 10 hours, and the decline in the amount of synthesized material after 5 hours.

Example 6.1

The BOD_5 of a waste water is determined to be 150 mg l⁻¹ at 20°C. Find BOD_7 (which is used in Sweden to indicate biological oxygen demand) at 15°C. As natural conditions are simulated, the constants from section 2.6 are used not those valid for biological treatment methods.

Solution.

Since it is waste water, $K_1 = 0.35 \text{ day}^{-1}$ and $K_T = 1.05$ are used. The following equation is used (see section 2.6 equation 2.40): $L_t = L_0 * e^{-k_1 * t}$

150 mg i⁻¹ corresponds to $L_0 - L_5 = L_0$ (1-e^{-0.35*5}), which gives:





Fig. 6.14. Removal of organic inbalances by biomass in a batch operation. Reduction of total carbonanceous oxygen demand (%) = y versus time (hours).

The various biological treatment processes can be summarized as follows:

1. The conventional **activated-sludge process** (see Fig. 6.15) is defined as a system in which flocculated biological growth is continuously circulated and contacted with organic waste water in the presence of oxygen, which is usually supplied in the form of air bubbles injected into the liquid sludge mixture. The process involves an aeration step followed by sedimentation. The separated sludge is partly recycled back to be removed with the waste water. The following processes occur:

- a. Rapid adsorption and flocculation of suspended organics,
- b. Oxidation and decomposition of adsorbed organics, and
- c. Oxidation and dispersion of sludge particles.

Sometimes, depending on the retention time and amount of oxygen introduced, ammonium ions are oxidized to nitrate by nitrifying organisms. This is seen particularly during the summer, and is due to the influence of the temperature on the rate constant for the nitrification process (see section 2.6 and Table 6.8).

Activated sludge usually provides an effluent with a soluble BOD_5 of 10-20 mg/l. The process necessitates the treatment of excess sludge before disposal.

An activated sludge plant can be designed by use of mass-balance principles.

If we assume that

- 1. the activated sludge reactor can be considered a mixed-flow reactor (see section 2.3),
- 2. that the influent and effluent biomass concentrations are negligible compared to biomass in the reactor or in the waste sludge,
- 3. all reactions occur in the reactor, i.e. neither biomass production or food utilization occurs in the clarifier,

then at steady-state conditions, we have: Biomass growth = biomass out or by use of (6.14):

$$V * X \left(\mu_m \frac{S}{K_s + S} - k_d \right) = Q_W * X_W$$
 (6.18)

where V is the volume, Q_W flow of waste sludge and X_W the biomass concentration in this flow (kg m⁻³).

A mass balance at steady-state for the substrate gives:

Food in - food out = food consumed or by use of (6.16):

$$Q_0(S_0-S) = \frac{\mu_m * S}{a(S+K_S)} * X * V$$
 (6.19)

where Q_0 is the flow rate (m³ d⁻¹) and S_0 the concentration of food (substrate, BOD₅) in the influent (kg m⁻³).

By rearrangement of (6.18) and (6.19) we obtain

$$\mu_{m}^{*} \frac{S}{K_{S} + S} = \frac{Q_{W}^{*} X_{W}}{V^{*} X} + k_{d} = \frac{Q_{0}^{*} a}{V^{*} X} (S_{0} - S)$$
(6.20)

 V/Q_0 is the hydraulic retention time π and $V^*X/Q_W^*X_W$ is called the mean all-residence time, π_c .

By substituting π and π_{C} into (6.20), we get:

$$\frac{1}{\pi_c} = \frac{a(S_0 - S)}{X^* \pi} - k_d$$
(6.21)

This equation can be used to give design data for an acitvated sludge reactor. a is usually 0.3-0.7 and k_d usually 0.01-0.1 d⁻¹. a = 0.5 and k_d = 0.05 d⁻¹ are often used for municipal waste water. X is often chosen to be 2-8000 mg l⁻¹.



Fig. 6.15. Conventional activated-sludge plant.

Example 6.2

Design a activated sludge system for secondary treatment of 10,000 m³ d⁻¹ of municipal waste water with BOD₅ = 150 mg l⁻¹. A completely mixed

reactor is to be used to obtain an effluent of 10 mg $BOD_5 l^{-1}$. X = 3000 mg l^{-1} is chosen. Find also the mass of waste solid per day. High nitrification efficiency is desirable.

Solution.

A π_c = 10 days is chosen to give a high nitrification efficiency (see Fig. 6.35 in 6.3.3, where the relationship between sludge age and nitrification is shown). From (6.21) we have:

 $\frac{1}{10} = \frac{0.5 \ (0.15 - 0.01)}{3^{+} \pi} - 0.05 \qquad \text{or } \pi = 0.155$

Reactor volume: 10,000 * π = 1550 m³

As $\pi_c = 10 \text{ d} = \frac{V * X}{Q_W * X_W} = \frac{1550 * 3}{Q_W * X_W}$

 $QX_W = 465 \text{ kg d}^{-1}$

2. The extended aeration process works on the basis of providing sufficient aeration time for oxidizing the biodegradable portion of the sludge produced form the organics removed from the process. Fig. 6.16 shows the process schematically. The excess sludge in the process contains only non-bio- degradable residue remaining after total oxidation. The total BOD₅ provided by this process is 20 mg/l or less.

Oxidation ditches have been developed as self-sufficient structures for the extended aeration of waste waters from small communities. Fig. 6.17 demonstrates the principles of an oxidation from 1 to 3 days. No effluent is withdrawn until the water level in the channel has built up to the highest operation level. The influent is then cut off and the rotor stopped. Solids are allowed to settle for an hour or two, then the clarified supernatant is withdrawn through an effluent launder, and, if desired, excess sludge is lifted from a section of the ditch to drying beds. The effluent is then cut off and the operation routine is repeated. Because, the solids are well stabilized during the long aeration time, they are no longer putrescent and water is readily removed from them. The fact that the sludge is well stabilized may allow it to be discharged into the receiving water with the effluent, provided the overall loading resulting from effluent and sludge can be accepted.



Fig. 6.16. Extended aeration process.



Fig. 6.17. Oxidation ditch.

3. In the contact stabilization process the waste water is aerated with stabilized sludge for a short period of 1/2 - 1 hour. The mixed liquid is then separated by sedimentation and when settled the sludge is transferred to a sludge stabilization tank where aeration is continued to complete the oxidation. This process is used to advantage when a high percentage of BOD is removed rapidly by bioadsorption after contact with the stabilized sludge. The extent of removal depends on the characteristics of the sludge and of the waste water. As general rule the process should give an efficiency of 85% BOD₅ removal.

4. A trickling filter is a bed packed with rocks, although, more recently, plastic media have been used. The medium is covered with a slimy microbiological film. The waste water is passed through the bed, and oxygen and organic matter diffuse into the film where oxidation occurs. In many cases recirculation of the effluent improves the BOD removal, especially when the BOD of the effluent is relatively high. A high-rate trickling filter provides an 85% reduction of BOD for domestic sewage, but 50-60% is the general figure for BOD_5 reduction in the treatment of organic industrial waste water.

A plastic-packed trickling filter will require substantially less space than a stone-packed one due to its bigger depth and specific surface area. According to Wing et al. (1970), plastic media packed to a depth of 6.5 m in a trickling filter will require less than one-fifth of the land required by those packed with stones to the usual depth of 2-4 m.

The specific surface area of rock-trickling filters is $40-70 \text{ m}^2/\text{m}^3$ and void space 40-60%, while plastic filters have a specific surface of $80-120 \text{ m}^2/\text{m}^3$ or even more, with a void space of 94-97%.

The design of biotowers is based on the following equation:

$$\frac{S_{e}}{S_{a}} = \frac{e^{-k^{*}D/Q^{n}}}{(1+R) - R^{*}e^{-k^{*}D/Q^{n}}}$$
(6.22)

where S_e is the effluent substrate concentration BOD_5 (mg l⁻¹), S_a is the BOD_5 of the mixture of raw and recycled mixture applied, D is the depth, Q the hydraulic loading ($m^2/(m^3 min)$), k treatability constant related to the waste water (min⁻¹), n is a coefficient related to medium characteristics. R is ratio of the recycled flow to the influent flow. S_a is found from a simple mass balance as:

$$S_a = \frac{S_0 + R \cdot S_e}{1 + R}$$
 (6.23)

where S_0 is the BOD₅ of the raw sewage (influent).

k is from 0.01 to 0.1 at 20°C. For municipal waste water, 0.055 min⁻¹ (20°C) is often used. n can be taken as 0.5 if not known from pilot-plant analysis. k is temperature dependent, see equation (6.17) and Table 6.8.

Example 6.3.

Design a biotower (trickling filter) composed of a modular plastic medium. 10,000 m³ d⁻¹ municipal waste water with a BOD₅ of 150 mg l⁻¹ must be treated. The temperature is 25°C, the depth of the tower is 6.5 m and the unit should be designed to produce an effluent of 10 mg l⁻¹.

Solution. R = 2 is chosen. (R = 1.5 or 3 could also be tested)

 $S_a = \frac{150 + 2 * 10}{1 + 2} = 56.7 \text{ mg } l^{-1}$

 $k_{25} = k_{20} * (1.035)^{25 \cdot 20} = 0.055 * (1.035)^5 \approx 0.065 \text{ min}^{-1}$ Equation (6.22) is used:

 $\frac{10}{56.7} = \frac{e^{-0.065^{\circ}6.5/Q^{0.5}}}{(1+2) - 2^{\circ}e^{-0.065^{\circ}6.5/Q^{0.5}}}$

Q is found to be 0.20 m^2/m^3 min. 10,000 $m^3 d^{-1} = 6.95 m^3 min^{-1}$

Surface area must therefore be $\frac{6.95}{0.2}$ m² = 34.8 m².

The unit has a depth of 6.5 m and if it is square, the dimensions are $\sqrt{34.8} = 5.9$ m. The tower is 5.9 ° 5.9 ° 6.5 m³.

5. Lagoons are the most common methods of organic waste treatment, when suficient area is available. They can be divided into four classes:

- a. Aerobic algal ponds, which depends upon algae to provide sufficient oxygen.
- b. *Facultative ponds*, which have an aerobic surface and an anaerobic bottom.
- c. *Anaerobic ponds,* which are loaded to such an extent that anaerobic conditions exist throughout the liquid volume.
- d. Aerated lagoons, which are basins where oxidation is accomplished by mechanical or diffused aeration units and induced surface aeration. The turbulence is usually insufficient to maintain solids in suspension, thus

most inert solids settle to the bottom where they undergo anaerobic decomposition. The basin (2-4 m deep) may include a sedimentation compartment to yield a more clarified effluent. If the turbulence level in the basin is increased to maintain solids in suspension, the system becomes analogous to an activated-sludge system.

An aerated lagoon can provide an effluent with less than 50 mg/l BOD_5 , depending on the temperature and the characteristics of the waste water. Post-treatment is necessary when a highly clarified effluent is desirecd, and large areas are required compared with the activated sludge process.

A pond can be designed in accordance with the mass-balance equations given in section 2.3. Equation (2.12) can be applied, or if several ponds are arranged in series, equation (2.13) is valid. If 50% efficiency of aeration is foreseen, what would be the needed oxygen supply?

Example 6.4.

A waste water flow of 500 m³/d from a small community is treated by use of 4 ponds in series. How large must the ponds be to remove 90% BOD_5 when the average BOD_5 is 200 mg l⁻¹ and the temperature is 18°C?

Solution. $K_1 (20^{\circ}C) = 0.35 \text{ day}^{-1}$ (see Table 2.18) O = 1.06 (see areated lagoons, Table 6.8) $K_T = K_{18^{\circ}} = 0.35 * 1.06^{-2} = 0.31$ $\frac{C_{im}}{C_{io}} = \frac{1}{10} = (\frac{1}{1+0.31 * \text{ tr}})^4$ $(1 + 0.31 * \text{ tr})^4 = 10$ 1 + 0.31 * tr = 1.78 tr = 2.52Each of the 4 ponds should have a volume of 2.52 * 500 = 1258 m³. If a depth of 1.5 m is used, the area will be 839 m² * 4 = 3356 m².

The oxygen must most probably be supplied by aeration, i.e. a minimum of

180 * 5000 = 900 kg/day or, if an efficiency of only 50% is assumed, 1800 kg/day.

6. Anaerobic digestion. The anaerobic breakdown of organic matter to harmless end-products is very complicated. Fig. 6.18 summarizes some of the more general processes.

Carbohydrate	Acetic acid	 CH₄
Fats	and other organic	CO₂
Proteins	acids	H₂S

Fig. 6.18. Anaerobic degradation of organics.

Methane-producing organisms convert long-chain volatile acids to methane, carbon dioxide and other volatile acids with a short carbon chain, which are then fermented in a similar fashion. Acetic acid is directly converted into carbon dioxide and methane. The rate of methane fermentation controls the overall reaction rate. Sufficient time must be available in the reactor to permit growth of the organisms or they will be washed out of the system. This means that the retention time must be greater than that corresponding to the growth rate of the methane-producing organisms. It is possible, by the use of extracellular enzymes, to cut down the resistance time considerably, but the use of such enzymatic processes is still only in its infancy.

Many factors, such as the composition of the sludge and the waste water. pH and temperature, influence the reaction rate, but it is generally shown that the overall rate is controlled by the rate of conversion of volatile acids to methane and carbon dioxide. Digestion fails to occur when there is an inbalance in the rate of the successive processes, which might result in a build-up of volatile acids. The optimum conditions can be summarized as follows: pH 6.8-7.4; redox potential -510 to -540 mV; concentration of volatile acids 50-500 mg/l; alkalinity (as calcium carbonate) 1500-5000 mg/l; temperature 35-40°C.

It should be possible to obtain effective digestion with a retention period as low as 5 days, but increasing the retention time to 10 days should assure 90% degradation of organic matter. Anaerobic digestion is used for the treatment of sludge form biological processes as well as for the treatment of industrial waste water with an extremely high BOD_5 , e.g. industrial waste water from the manufacture of yeast.

The major part of the gas produced by anaerobic treatment processes comes from the breakdown of volatile acids. The gas is composed of methane, carbon dioxide, hydrogen sulphide and hydrogen. The higher the resistance time, the lower the percentage of carbon dioxide and the higher the percentage of methane in the gas produced.

Lawrence and McCarty (1967) have shown that methane gas production, at a good approximation, is 0.4 m³ gas per kg BOD removed. This value must be considered as the maximum obtained by complete conversion of the solid into methane.

7. Effective nitrification occurs when the age of the sludge is greater than the growth rate of the nitrofying micro-organisms. Further details on this process, see 6.3.3.

8. Nitrate can be reduced to nitrogen and dinitrogen oxide by many of the heterotrophic bacteria present in activated sludge. For further details, see 6.3.3.

6.2.4 Mechanico-biological treatment systems.

Many variations in flow pattern for mechanico-biological systems, are used in the treatment of municipal waste water.

Fig. 6.19 shows a flow diagram of a conventional activated-sludge plant.



Fig. 6.19. Flow diagram of a conventional activated-sludge plant. (see Table 6.9).

In the process sewage is mixed with a portion of returned activatedsludge to facilitate the primary settling (improved flocculation). For typical municipal sewage an aeration time of 4-6 hours must be applied, if a BOD_5 removal of 90% or more is required. Table 6.9 gives some typical results.

Trickling filters are generally used at smaller sewage treatment plants (1000 - 10,000 inhabitants). They are classified according to the hydraulic and organic loading used, see Table 6.10.

TABLE	6.9					
Typical	results	obtained	from	activated-sludge	plant	(mg/l)

	1	2	3
BOD ₅	150 - 300	100 - 180	15 - 20
Suspended matter	50	5 - 10	2 - 8
N _{total}	25 - 45	22 - 40	18 - 32
P _{total}	6 - 12	6 - 12	5 - 10

Numbers refer to Fig. 6.19

TABLE 6.10 Trickling filters

	Low-rate operation	High-rate operation
Hydraulic loading (m ³ /m ² /24h) Process loading (kg/m ³ /24h)	1 - 4 0.2 - 1.5	8 - 40 2 - 20
Depth (m) Single stage Multi stage	1.5 - 3 0.7 - 1.5	1 - 3 0.5 - 1.5
Relative recirculation in term of inflow	<u>, , , , , , , , , , , , , , , , , , , </u>	0.5 - 10
BOD ₅ -removal Suspended solid removal	85 - 90% 90 - 95%	75 - 85% 80 - 90%

A combination of an activated-sludge plant and a trickling filter is often applied where high quality effluent is required. In addition to a 95% or more BOD_5 -removal, 80-90% nitrification of ammonia will take place, except perhaps during the winter (the nitrification process is highly dependent on temperature, see Table 6.8). Fig. 6.20 illustrates an example of a sewage plant using such a two-step biological treatment.

Lagoons are only used where considerable space is available, and as, in most cases, they do not give an effluent of sufficient quality by today's standards, this method is now used less and less. Table 6.11 summarizes design factors and results for lagoons.

The final selection of biological treatment method is highly dependent on

the receiving water, which determines the acceptable BOD_5 of the effluent, see section 2.6.



Fig. 6.20. Sewage plant combining trickling filter and activated sludge treatment.

TABLE	6.11		
Design	factors	for	lagoons

.

	Aerobic	Facultative	Anaerobic	Aerated
Depth (m) Retention time	0.2 - 0.4	0.75 - 2	2.5 - 4	2 - 4
(days)	2 - 6	7 - 30	30 - 50	2 - 10
(kg/ha/day)	100 - 200	20 - 50	300 - 500	depending upon waste charac- teristics and aeration
BOD removal (%)	80 - 90	75 - 85	50 - 70	50 - 90

6.2.5 Other methods used for BOD-removal.

Mechanico-biological systems are widely used for BOD removal, but other methods are also available for the treatment of municipal and industrial waste waters - combinations of physico and chemical methods and irrigation. They are relatively more attractive for the treatment of waste water with high BOD_5 , such as waste water from the food industry, but can also be used on municipal waste water.

It is difficult to provide guidelines on when physico-chemical methods are more advantageous than mechanico-biological ones, but the following issues should be considered:

- 1. Physico-chemical methods are not *susceptible to shock loadings* and the presence of toxic compounds.
- 2. The space required for physico-chemical methods is, in most cases, less than for mechanico-biological treatment plants.
- 3. Recovery of fat, grease and proteins can be achieved using physicochemical methods in the treatment of waste water from the foodprocessing industry.
- 4. Although operation costs are slightly higher for physico-chemical methods, investment cost will generally be lower.

P.6.7. The following physico-chemical methods are used for BOD-reduction: chemical precipitation, ion exchange, adsorption and reverse osmosis.

Apart form obtaining a substantial reduction of the phosphate concentration organic matter is also precipitated, by using lime, aluminium sulphate or iron(III) chloride, due to a reduction of the zetapotential of organic flocs (Balmer et al., 1968). Normally a direct precipitation on municipal waste wate4r will reduce the potassium permanganate number and the BOD_5 by 50-65%, which has to be compared with the effect obtained by plain settling without the addition of chemicals (Davidson and Ullman, 1971). Furthermore, precipitants (lignosulphonic acid, activated bentonite and glucose sulphate) have been developed for precipitation of proteins, permitting their recovery from food-processing industries (see Tønseth and Berridge, 1968 and Jørgensen, 1971).

lon exchangers are able to take up ionic organic compounds, such as polypeptides and amino acids. Macroporous ion exchangers are even able to remove protein molecules from waste water. Cellulose ion exchangers designed for protein removal have been developed (Jørgensen, 1969, 1970 and 1973). They are inexpensive compared with other ion exchangers and are highly specific in uptake of high molecular weight ions.

Adsorption on activated carbon can remove not only refractory organic

compounds (see 6.4.3), but also biodegradable material. This has been used for the treatment of municipal waste water (see below).

Reverse osmosis is an expensive waste water treatment process, which explains why its application has been limited to cases in which other processes are inappropriate or where recovery is possible. The process has been used to recover proteins from whey, which could not be treated by conventional methods, because of its high concentration of proteins and carbohydrates. Table 6.12 summarizes the results of this application.

TABLE 6.12 Reverse osmosis of whey

	Dry matter	Protein	Lactose	Ashes
Whey (%)	6.4	0.8	4.4	0.7
Concentrate (%)	29.0	3.6	23.0	2.2
Permeate (%)	0.15	0.06	-	0.1

The applications of purely physico-chemical methods for BOD-removal are best illustrated by some examples. The so-called Guggenheim process uses chemical precipitation with lime and iron sulphate followed by a treatment on zeolite for ammonia removal (Gleason and Loonam, 1933). A 90% removal of BOD_5 , phosphate and ammonia is achieved (Culp, 1967 and 1967a).

A combination of chemical precipitation by aluminium sulphate and ion exchange on cellulose ion exchangers and clinoptilolite also seems promising for the treatment of municipal waste water. 90% removal of BOD_5 and ammonia is obtained in addition to 98% removal of phosphate and suspended matter (see Jørgensen, 1973 and 1976).

The so-called AWT system is a combination of precipitation with lime and treatment on activated carbon. Zuckerman and Molof (1970) claim that by using lime the larger organic material is hydrolysed, giving better adsorption because activated carbon prefers molecules with a molecular weight of less than 400. A flowchart of this process is shown in Fig. 6.21.

Fig. 6.22 is a flow diagram of the combination of chemical precipitation and ion exchange used in the treatment of waste water from the food industry (Jørgensen, 1968, 1969, 1973 and 1978). This process allows recovery of fat, grease and proteins. Table 6.13 gives the analytical data obtained when this process was used on waste water from herring filetting after centrifugation of the raw waste water to recover fish oil. Table 6.14 gives a before and after analysis of this process for waste water from an abattoir. For comparison the table also includes the results obtained from using a biological plastic filter.



Fig. 6.21. The AWT system consists of 1) mechanical treatment, 2) settling after chemical precipitation, 3) treatment on activated carbon, 4) filtration.



Fig. 6.22. Recovery of proteins (+ grease).

In addition to mechanico-biological treatment or a combination of physico-chemical methods

P.6.8. the use of spray irrigation can also be considered as a solution to the problem of the biological oxygen demand of waste water.
Spraying and irrigation of waste water onto fields and meadows is widely considered to be the best and cheapest way of treating waste water from the food-processing industry. The industry favours this solution as it ensures maximum utilization of the fertilizing properties of these waste waters (Sanborn, 1953).

 TABLE 6.13

 Analytical data of waste water from herring filetting

	Raw waste water	After cen- trifuga- tion 1. step	After chem. precipi- tation 2. step	After Cel- lulose ion- exchanger 3. step
BOD ₅ (mg/l)	11000	5800	2000	1100
N (mg/l)	180	162	60	23
Suspended matter (mg/l)	400	170	40	2
KMnO ₄ (mg/l)	8000	4000	1200	600

TABLE 6.14

Analysis of waste water from an abattoir (mg/l)

	Raw water	After biolo- gical plastic filter	After chem. precipitation (glucose sul- phate is used)	After chem. precipitation and ion ex- change
BOD ₅	1500	400	600	50
KMnO ₂	950	350	460	60
Total N	140	42	85	15
HN ₃ -N	20	15	18	2
NO ₃ -N	4	5	4	1
P	45	38	39	1.5

As early as 1942 an outline of the agricultural use of waste water from dairies was published.

Raw waste water was stored for 5-6 hours in a tank situated on an irrigated area. Irrigation was recommended at a rate of 150-400 mm/year or 75-200 m^3 /day of effluent per ha of irrigated fields.

The storage tank should be cleaned continuously, by means of compressed air for example. After irrigation the tanks and pipes should be rinsed with fresh water in an amount equal to 1/3 of the daily discharge of the waste water.

The method is not usually recommended in areas subject to persistent frosts, or where the soil has a natural high moisture content or a high ground water level (see further below).

Spraying the waste water on pastures carries the risk of affecting cattle

with tuberculosis. Therefore a period of 14 days is recommended between irrigation and putting cows out to pasture. The limitations of this process can be summarized as follows (Eckenfelder et al., 1958).

1. Depth of the ground water.

The quantity of waste water that can be sprayed onto a given area will be proportional to the depth of the soil through which the waste water must travel to the ground water. A certain soil depth must be available if the contamination of the ground water is to be avoided.

2. Initial moisture content.

The capacity of the soil to absorb is dependent on its initial moisture content.

Sloping sides will increase the runoff and decrease the quantity of water which can be absorbed by a given area.

3. Nature of the soil.

Sandy soil will give a high filtration rate, while clay will pass very little water. A high filtration rate will give unsufficient biological degradation of the organic material and too low a filtration rate will reduce the amount of water which can be absorbed by a given area.

P.6.9. The capacity is proportional to the coefficient of permeability of the soil and can be calculated by the following equation: Q = K * N (6.24)

where Q = the quantity of water (m^3) which can be absorbed per m² per 24h; K = the permeability coefficient, expressed as m/24h; N = the saturation of the soil for which a value of 0.8-1.0 can be used in most cases.

If the soil has different characteristics at different depths an overall coefficient can be calculated:

$$K = \frac{H}{H_1/K_1 + H_2/K_2 + \dots + H_n/K_n}$$
(6.25)

where H = the total depth and H₁, H₂..... H_n = the depth of the different types of soil with permeability coefficients K₁, K₂, etc.

Table 6.15 gives the permeability coefficients for different soil types (Eckenfelder et al., 1958).

In addition to soil properties several characteristics require consideration in a spray irrigation system. Suspended matter must be removed by screening or by sedimentation before the water is sprayed. Otherwise the solids will clog the spray nozzles and may mat the soil surface rendering it impermeable to further percolation (Canham, 1955). The pH must be adjusted as excess acid or alkali may be harmful to crops.

High salinity will also impair crop growth. A maximum salinity of 0.15% has been suggested to eliminate this problem (U.S. Department Agricultural Handbook, 1954).

TABLE 6.15Permeability coefficients for different soil types

Description	Permeability (m per 24h)	_
Fine sand Trace silt Light agricultural soil 50% clay and 50% organic soils Predominating clay soil	100 - 500 15 - 300 1 - 5 0.15 - 0.40 < 0.1	_

Spray irrigation has been succesfully used for waste water from dairies, pulp and paper industries (Gellman et al., 1959; Wisneiwski, 1956), cannery waste (Luley, 1963; Williamson, 1959) and fruit and vegetable processing plants.

The data from various spray irrigation plants are given in Table 6.16.

TABLE 6.16Data from spray irrigation plants

Waste water from the manufacture of:	Loading kg BOD ₅ per year	Application rate (m/year)
Asparagus and beans	30	5
Tomatoes	600	3
Starch	750	3
Cherries	700	1.6
Paperboard and hardboard	500	1.6

Disposal of industrial waste water by irrigation can be carried out in several ways:

- 1. Distribution of the water over sloping land with a runoff to a natural water source.
- 2. Distribution of the water through spray nozzles over relatively flat terrain.
- 3. Disposal to ridge and furrow irrigation channels.

6.3. NUTRIENT REMOVAL.

6.3.1. The eutrophication problem and its sources.

The word eutrophication means nutrient rich, which is generally considered to be undesirable due to:

- 1. the green colour of eutrophic lakes makes swimming and boating more unsafe,
- 2. an aesthetic point-clear water is preferred to turbid water,
- 3. the oxygen content of the hypolimnion is reduced due to decomposition of algae, especially in the autumn, but also in the summer, when the stratification of deeper lakes is most pronounced.

The eutrophication is, however, not controlled merely by determining the limiting element or elements and then reducing their concentration in the discharged waste water - the problem is far more complex (see section 2.7).

It is important to consider the sources of the nutrients and for a balanced overview of the situation a mass balance must be set up for each case (see principle 2.23).

However, in some situations it is not possible to obtain the necessary data for setting up a mass balance. In these cases the information given in Table 6.17 can be used. This table also illustrates the relative importance of the three sources of nutrient input to receiving waters, showing that a significant input of nitrogen originates from land and precipitation. This is the general picture, but it is not always valid and should only be used in a data-poor situation.

The role of forest fertilization as a source of nutrients has been examined by Rouger (1981). His results we summarized in appendix 9.

Schindler (1971) has shown that midsummer maximum productivity and midsummer maximum biomass increase linearly with $(A_d + A_1)/V$, where A_d is the watershed area, A_1 the lake area and V the lake volume. This is in accordance with Table 6.17, as the P- and N-loading is proportional to the watershed area and lake area and by division by the volume, the nutrient concentration results, which again determines the maximum productivity and biomass.

Phosphorus is mainly derived from sewage, although the input from agriculture in some cases may also be significant. It is often difficult to control the input of nitrogen to an ecosystem. Such processes as nitrogen fixation by algae may also play a major role.

Control of the eutrophication of lakes requires removal of one or more nutrients from waste water, and the final decision as to the right management strategy - what nutrient should be removed and to what extent - implies the use of ecological models, see Jørgensen (1976, 1980 and 1981) and Jørgensen et al. (1978).

A simple model might, however, be the right model in a data-poor situation.

TABLE 6.17 Sources of nutrients

A: Export scheme of phosphorus E_P and nitrogen E_N (mg m⁻²y⁻¹) ¹)

	F		E.	······
Land use	Geologi Igneous	cal classification Sedimentary	Geologica Igneous	classification Sedimentary
<u>Forest_runoff</u> Range Mean	0.7 - 9 4.7	7 - 18 11.7	130 - 300 200	150 - 500 340
<u>Forest + pasture</u> Range Mean	6 - 16 10.2	11 - 37 23.3	200 - 600 400	300 - 800 600
<u>Agricultural areas</u> Citrus Pasture Cropland	11 15 - 22 -	8 - 75 - 100	22 100 500	40 - 850 - 1200

B: Nutrient concentration in rain water (mg I-1) 2)

	C _{PP}	C _{NP}	
Range	0.015 - 0.1	0.3 - 1.6	
Mean	0.07	1.0	

C: Artificial P- and N-loads

The discharge per capita per year is 800-1800 g P and 3000-3800 g N in industrialized countries. If possible, local values should be applied.

The figures are based on an interpretation of the following references: ¹⁾ Dillon and Kirchner (1975), Lønholt (1973) and (1976), Vollenweider (1968) and Loehr (1974). ²⁾ Schindler and Nighswander (1970), Dillon and Rigler (1974), Lee and Kluesener (1971) and Jørgensen et al. (1973).

Example 6.5

A lake has a surface area of 5 km^2 and a catchment area of 60 km^2 , mainly agricultural. The average depth of the lake is 5 m. It receives an annual precipitation of 0.8 m and mechanical-biologically treated waste

water from 10,000 inhabitants.

Set up an approximate mass balance for the lake and suggest, based on Fig. 2.39, what should be done to reduce its eutrophication.

Solution.

 E_P and E_N are chosen to be 80 mg m⁻²y⁻¹ and 900 mg m⁻²y⁻¹, respectively (see Table 6.17).

Thi	s gives an annual	inț	out of:	
Α.	Runoff	:	P-input 80 \cdot 60 \cdot 10 ⁶ mg = 4800	kg
			N-input 900 • 60 • $10^6 \text{ mg} = 54000$	kġ
В.	Precipitation	:	P-input 0.07 * 0.8 * 5 * 10^6 g = 280	kg
			N-input 1 * 0.8 * 5 • $10^6 = 4000$	kĝ
C.	Waste water	:	100 m ³ /inh. 10 mg l ⁻¹ P 30 mg l ⁻¹ N corresp. to 1000 g P/inh. and 3000 g N (compare with Table 6.17 C) P-input: 10000 kg N-input: 30000 kg	

About 2/3 of P-input comes from waste water, while only about 1/3 of N-input comes from this source.

The total P-loading at present corresponds to:

 $\frac{(4800 + 280 + 10000) \cdot 10^3}{5 \cdot 10^6} \text{ g P/m}^2 \text{ y} \quad (\text{see Fig. 2.39})$

 \approx 3 g P/m² y: A very high value.

A considerable improvement could be expected if the P-input from waste water were to be reduced by 90-99% (see Fig. 2.39).

The removal of nitrogen would not reduce the eutrophication correspondingly. A **simultaneous** removal of nitrogen would not improve the conditions, as:

- 1. 58,000 kg would still be the input and this is more than 10 times as much as the P-input after P-removal. The use of P and N by algae is estimated to be in the ratio of 1:9 (see Table 2.22).
- 2. Nitrogen-fixing algae might be present in the lake.

In addition to the eutrophication problem discharge of nitrogen

compounds into receiving waters can cause two environmental problems:

1. Ammonium compounds may be nitrified, influencing the oxygen balance in accordance with the following equation:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$$
 (6.26)

Municipal waste water, which is treated by a mechanico-biological method, but not nitrified, will normally contain approximately 28 mg ammonium-nitrogen per litre. In accordance with equation 6.18, this concentration might cause an oxygen consumption of 128 mg oxygen (see also section 2.7 and principle 2.16).

- 2. Ammonia is toxic to fish as mentioned in sections 2.4 and 4.7.
- P.6.10. Under all circumstances methods for the removal of both nitrogen and phosphorus must be available,

and these methods are discussed in the following paragraphs.

P.6.11. Phosphorus can be removed by chemical precipitation or ion exchange, while nitrogen can be removed by nitrification + denitrification, ammonia-stripping, ion exchange or oxidation by chlorine followed by treatment on activated carbon. Both nutrients can be removed using algal ponds.

6.3.2. Chemical precipitation of phosphorous compounds.

Chemical precipitation is widely used as a unit process for the treatment of waste water.

Municipal waste water is treated by precipitation with: aluminium sulphate $(Al_2(SO_4)_3, 18H_2O)$ calcium hydroxide $(Ca(OH)_2)$ or iron chloride $(FeCl_3)$ for removal of phosphorus.

When chemical precipitation is combined with a mechanico-biological treatment, the precipitation can be applied after the sand-trap using the primary settling for sedimentation, simultaneously with the biological treatment or after a complete mechanico-biological treatment. In these cases the precipitation is described respectively as, *direct precipitation, simultaneous precipitation and a post-treatment*, see Figs. 6.23, 6.24 and 6.25.



Fig. 6.23. Direct precipitation.



Fig. 6.24. Simultaneous precipitation. Recirculation of sludge is not shown.



Fig. 6.25. Post-treatment.

Lately chemical precipitation has become popular in the treatment of municipal waste water in Sweden, U.S.A., Switzerland and other countries. However, the process was already in use for this purpose in Paris in 1740 and in England more than 100 years ago. Just before the Second World War, Guggenheim introduced the process as a treatment preceeding an activated-sludge plant (Rosendahl, 1970). However, the method did not find favour until the late 1960s due to the cost of chemicals and to the low reduction in BOD_5 , which was supposed to be the major concern.

The main objective of applying chemical precipitation is the removal of phosphorus for the control of eutrophication. The efficiency of phosphorus removal is generally between 75 and 95% (Statens Naturvårdsverk, 1969). However, in addition to this effect, chemical precipitation can also achieve the following:

- 1. Substantial *reduction in the number of microorganisms*, particularly when calcium hydroxide is used (Buzell, 1967).
- 2. Reduction in BOD₅ of 50-65% (Buzell, 1967).
- 3. *Reduction of non-biodegradable material* (so-called refractory material) in the same ratio as bio-degradable material (Jørgensen, 1976).
- 4. *Reduction in the concentration of nitrogenous compounds* due mainly to the removal of organic compounds.
- 5. A reduction in heavy metal concentration, which is essential (see also 6.5.2 and Nilsson, 1971).

P.6.12. The removal of phosphorus entails the use of three chemicals: aluminium sulphate, iron(III) chloride and calcium hydroxide.
As the composition of waste water and the cost of the chemicals vary from place to place, it is difficult to give a general recommendation on the choice of chemicals. It seems necessary to examine each case separately, although it is possible to draw some conclusions and set up some general guidelines.

Municipal waste water contains orthophosphate, and other phosphorus species. Table 6.18 shows the approximate concentration of the major phosphorous compounds. pH also influences the phosphorous species as demonstrated in Fig. 6.26.

TABLE 6.18

Approximate concentrations in typical raw domestic sewage

Form	mg P I ⁻¹	<u></u>
Total Orthophosphate Tripolyphosphate Pyrophosphate Organic phosphate	10 5 3 1 ≤1	

Source: Jenkins et al. (1971)

The chemical precipitations form insoluble compounds with phosphorus species, but the solubility is naturally dependent on pH, as shown for the most important precipitated compounds in Fig. 6.27.



Fig. 6.26. -log conc. mol/l, phosphates. Plotted to pH. Reproduced from Jenkins et al., 1971.

For aluminium and iron phosphates the pH dependence is probably explained to a certain extent by the following process:

$$(MePO_4)_n + 3OH^- - Me_n(OH)_3(PO_4)_{n-1} + PO_4^{3-}$$
 (6.27)

Increasing OH concentration will effect this process to the right causing dissolution of the precipitated phosphate.

The precipitation of phosphates using calcium hydroxide is based on the formation of $Ca_{10}(PO_4)_6(OH)_2$, which will involve a high pH value: 10.5 - 12.0 (Nilsson, 1969).

However, many of the processes interact, and the phosphate species are able to form complexes with some metal ions, thereby significantly increasing phosphate stability. Table 6.19 shows some of the more important processes which may influence precipitation.



Fig. 6.27. The solubility of phosphate salts as a function of pH. Reproduced from Stumm and Leckie, 1970.

Aluminium sulphate is the precipitant most widely used in Scandinavia, where a technical grade named AVR is used. In Table 6.20 the composition of AVR is compared with an iron-free quality (Boliden, 1967 and 1969).

Equilibrium	Log equilibrium constant 298°K
$\begin{array}{l} H_{3}PO_{4} = H^{+} + H_{2}PO_{4}^{-} \\ H_{3}PO_{4}^{-} = H^{+} + HPO_{4}^{2} \\ HPO_{4}^{2^{-}} = H^{+} + PO_{4}^{3^{+}} \\ HPO_{4}^{2^{-}} = H^{+} + HO_{4}^{3^{+}} \\ H_{3}P_{2}O_{7}^{-} = H^{+} + H_{2}P_{2}O_{7}^{2^{-}} \\ HPO_{7}^{2^{-}} = H^{+} + HP_{2}O_{7}^{3^{-}} \\ HP_{2}O_{7}^{2^{-}} = H^{+} + HP_{3}O_{12}^{3^{-}} \\ HP_{3}O_{10}^{2^{-}} = H^{+} + HP_{3}O_{12}^{3^{-}} \\ HP_{3}O_{10}^{2^{-}} = H^{+} + HP_{3}O_{12}^{3^{-}} \\ HP_{3}O_{10}^{2^{-}} = H^{+} + HP_{3}O_{12}^{5^{+}} \\ Ca^{2^{+}} + PO_{4}^{3^{-}} = CaPO_{4}^{0} \\ Ca^{2^{+}} + HPO_{4}^{2^{-}} = CaHPO_{4} \\ Ca^{2^{+}} + HPO_{4}^{2^{-}} = CaHPO_{4} \\ Ca^{2^{+}} + HPO_{4}^{-^{-}} = CaH_{2}O_{7}^{2^{-}} \\ Ca^{2^{+}} + HP_{2}O_{7}^{3^{-}} = CaHPO_{4} \\ Ca^{2^{+}} + HP_{2}O_{7}^{3^{-}} = CaHP_{2}O_{7}^{-} \\ Ca^{2^{+}} + HP_{3}O_{10}^{5^{-}} = CaP_{3}O_{10}^{3^{-}} \\ Ca^{2^{+}} + HP_{3}O_{10}^{3^{-}} = CaHP_{3}O_{10}^{3^{-}} \\ Ca^{2^{+}} + HP_{3}O_{10}^{3^{-}} = CaH_{2}P_{3}O_{10}^{-} \end{array}$	-2.1 -7.2 -12.3 -2.5 -6.7 -9.4 -2.3 -6.5 -9.2 6.5 2.7 1.4 5.6 3.6 8.1 3.9 3.9

TABLE 6.19 Phosphate equilibria (Source: Sillen and Martell (1964))

TABLE 6.20 Composition of AVR compared with an iron-free quality

	Composition Iron-free	percentage AVR	
Al ₂ O ₃ total	17.1	15.1	
Fe ₂ O ₃ Fe Water insoluble	0.01 0 0.05	2.1 0.2 2.5	
H ₂ O, chemical pH 1% water soluble	43.7 3.6	43.9 3.6	
Size (mm)	0.25 - 2.0 granular	0.25 - 2.0 granular	
Weight kg/l	0.90	0.95	

The relationship between the addition of AVR-quality aluminium suphate and the phosphorus concentration in municipal waste water is shown in Fig. 6.28 for different concentrations of phosphorus in the treated water. The dose of the chemical depends on the phosphorus concentration in the waste water and on the required concentration in the treated water (Nilsson and Isgard, 1971).



Fig. 6.28. The dependence of AVR addition on the P concentration of the waste water and the desired P concentration, indicated as C. Source: Gustafson and Westberg (1968).

P.6.13. The relationship, that describes the effect of chemical precipitation, can be interpreted by the Freundlich Adsorption isotherm: (see Fig. 6.28)

$$\frac{C_{o} - C}{n} = a * C^{b}$$
(6.28)

where

 C_0 = initial concentration of P (mg l⁻¹)

C = final concentration of P (mg l⁻¹)

 $n = dose of chemical mg l^{-1}$ Fe or Al

a and b = characteristic constants

The constants a and b can be found in Table 6.21.

TABLE 6.21 a and b in Freundlich's aluminium sulphate an	s adsorptio d iron(III)	on isotherm chloride	for
Precipitation with	a	b	
Aluminium sulphate Iron(III) chloride	0.63 0.26	0.2 0.4	

Example 6.6.

Find the dose of AI required to remove 90% P from waste water with a P-concentration of 10 mg l^{-1} and hypolimnic water with a P-concentration of 1 mg l^{-1} .

Solution.

$$\frac{C_{0} - C}{n} = a * C_{b}$$
or
$$n = \frac{C_{0} - C}{a * C^{b}} = \frac{C_{0} - C}{0.63 * C^{0.2}}$$
A. Waste water $C_{0} = 10$ $C = 1$

$$n = \frac{10 - 1}{0.63 * 1^{0.2}} = \frac{9}{0.63} = 14.3$$
B. Hypolimnic water $C_{0} = 1$ $C = 0.1$

$$n = \frac{1 - 0.1}{0.63 * 0.1^{0.2}} = \frac{0.9}{0.63 * 0.63} = 2.3$$

As seen, about 6 times as much precipitant is needed in case A, but 10 times more phosphorous is removed. In practice, even relatively more precipitant will be used in case B than the theoretical calculations show here.

The values given in Fig. 6.28 and Table 6.19 are based on the assumption that the pH is close to the optimum (for aluminium sulphate 5.5 - 6.5, for iron(III) chloride 6.5 - 7.5). The relationship between the efficiency and the pH is plotted in Fig. 6.29 under what we could call normal conditions, that is when the phosphorus concentration is about 10 mg l⁻¹, the concentration of different phosphorus species is as shown in Table 6.18 and the calcium concentration is 20 - 50 mg l⁻¹.

Some references mention pH optima other than that shown in Fig. 6.29. This discrepancy can probably be explained by a difference in calcium concentration (Gustafson and Westberg, 1968).

Iron(III) chloride is more expensive to use than aluminium sulphate, but

iron(II) sulphate is a waste product of the chemical industry and can easily be oxidized to iron(III) by the use of chlorine or by aeration, for instance in the activated-sludge process (Särkka, 1970). Therefore iron(II) sulphate has been widely used as a precipitant, especially for simultaneous precipitation.

The relationship between dose, phosphorus concentration and the final concentration in the treated water is similar to that for aluminium sulphate (see Fig. 6.30). The precipitation in this case also follows the Freundlich adsorption isotherm, but the constants a and b are different from those for aluminium sulphate.

As mentioned above the efficiency is dependent on pH and this relationship is also included in Fig. 6.29.

The efficiencies reported in the literature differ significantly more than those for aluminium sulphate, probably due to the difference in optimum pH (Thomas, 1965), but these observations might also be explained by the formation of complexes or a different ability to absorb or react chemically with the more comples phosphorus species.



Fig. 6.29. The relationship between the efficiency of precipitation with coagulants and the pH. (1) for aluminium sulphate, (2) for iron(III) chloride, (3) for calcium hydroxide. (1') and (2') is (1) respectively (2) by presence of calcium ions. Reproduced from Gustafson and Westberg (1969).



Fig. 6.30. The dependence of iron(III) salt addition on the P concentration of the waste water and the desired P concentration, indicated as C. Source: Gustafson and Westberg (1968).

Hydrated lime or calcium hydroxide is the cheapest of the three precipitants used for removal of phosphorus. However, greater amounts of calcium hydroxide are required to obtain a given efficiency. While 120 - 180 mg per litre of aluminium sulphate or iron(III) chloride are sufficient in most cases to achieve 85% removal or more, 2 to 5 times more calcium hydroxide will be needed.

For the precipitation of phosphorus compounds in waste water with aluminium sulphate and iron(III) chloride more than the stoichiometric amount is used, as pure orthophosphate is not precipitated, but adsorption is also involved. However, for calcium hydroxide precipitation a pH value of at least 10 is required to achieve a sufficiently high OH⁻ concentration.

P.6.14. Thus the amount of calcium hydroxide is determined by the alkalinity of the water.

(Alkalinity is a measure of the concentration of alkaline ions, mainly hydrogen carbonate and carbonate; it can be expressed as mg l^{-1} of calcium carbonate).

The practical relationship between the alkalinity and the mg of calcium hydroxide required to reach pH 11, which assure effective precipitation, is illustrated in Fig. 6.31. Most waste water has an alkalinity in the range of

150 - 300 mg calcium carbonate per litre, which, as can be seen from the figure, corresponds to about 300 to 480 mg calcium hydroxide per litre.





Generally higher efficiencies are obtained by precipitation with hydrated lime than by the other two precipitants - 90 - 95% efficiency being common in practice. The orthophosphate is precipitated with an efficiency of almost 100%, while polyphosphates are precipitated with more modest efficiency giving an overall efficiency close to 95%.

The disadvantage of precipitating with lime is the high pH, which makes an adjustment after the precipitation necessary. Carbon dioxide produced by incineration of the sludge can be used for this purpose (see Fig. 6.32), where the calcium oxide produced by the incineration is also reused to certain extent at the same time as the carbon dioxide is applied to adjust the pH. In this process the calcium oxide can be recycled 3 - 5 times corresponding to a more stoichiometric ratio between calcium and phosphate.

The calcium hydroxide produced in this manner can be used as fertilizers (Dryden and Stern, 1968).

The amount of sludge produced by chemical precipitation is dependent on several factors, of which the major factor is the dose of chemicals (see Table 6.22).

P.6.15. The sludge formed from the precipitation of phosphorus with aluminium sulphate can be treated together with anaerobic biological sludge, without difficulty, while that formed from the precipitation with iron compounds might be dissolved due to reduction of iron(III) to iron(II) phosphate, which can react in accordance with the following process:

 $Fe_3(PO_4)_2 + 3H_2S - 3FeS + 2H_2PO_4^- + 2H^+$ (6.29)

The same process occurs, when ironrich sediment releases phosphorus due to anaerobic conditions, see section 4.9.

TABLE 6.22

Additional sludge by precipitation D = dose expressed as g/m³ Al, Fe or hydrated lime

Chemical	Additional sludge in g per m ³ waste water	
Aluminium sulphate	4 D	
Iron(III) salt	2.5 D	
Hydrated lime	1 - 1.5 D	

P.6.16. Without a pH-adjustment the sludge produced by the calcium hydroxide precipitation can hardly be treated by anaerobic digestion. If the chemical sludge is mixed with a large volume of biological sludge the pH might be sufficiently low to allow an anaerobic treatment.

The same considerations are valid for an aerobic sludge treatment with the exception that the above-mentioned reduction of iron, of course, cannot take place.

Filtration, centrifugation or drying of chemical sludge do not cause any additional problems. Recirculation of sludge is practised in many plants and often means a reduced consumption of chemicals. Recovery of aluminium sulphate has even been suggested. By treatment of filtered sludge with sulphuric acid after aluminium sulphate precipitation the aluninium ions go into solution as aluminium sulphate, which can be reused. However, the economical advantage is in most cases too modest to pay for this extra process.



Fig. 6.32. Chemical precipitation with partial recirculation of calcium oxide and use of CO_2 from incineration for adjustment of pH.

Several heavy metals are removed quite effectively by precipitation. Aluminium sulphate is able to precipitate lead, copper and chromium with high efficiency, while cadmium and zinc are only precipitated partially. Iron-based chemicals produce the same effects at the same pH, but as the pH is often lower with this precipitation, in practice iron salts often give a lower efficiency than aluminium sulphate. Calcium hydroxide removes almost all heavy metals very efficiently, as most metal hydroxides have a very low solubility at pH 10-11. Calcium hydroxide is used (see 6.4.2) to remove heavy metals from industrial waste water.

The relationship between pH and the solubility for metal ions + metal hydroxide complexes is illustrated in Fig. 6.33 for 6 important metal ions. However, municipal waste water will often contain compounds that are able, through formation of complexes, to increase the solubility for most metal ions. This is demonstrated in Fig. 6.34, where the solubility of the same 6 metal ions is plotted against pH for a water containing NTA (Nitrilo Three Acetate), chloride and calcium ions.



Fig. 6.33. The solubility of pure metal hydroxides as a function of pH. (From Nilsson, 1971).

P.6.17. These additional effects of the precipitation process must not be overlooked. For treatment of municipal waste, it might also be important to precipitate toxic organics and heavy metals in addition to achieving a reduction of BOD₅ of approximately 60% and a 80-95% removal of phosphorus compounds.

If the municipal waste water contains more or less treated industrial waste water, in some cases it might be a better solution to use chemical precipitation rather than mechanical-biological treatment, depending on the receiving water. It seems worthwhile, at least as a primary step, to consider the chemical precipitation treatment of waste water for discharges to lakes or the sea.

The mentioned effects can, however, only be obtained by a current process control. An unacceptable efficiency results from:

1. Too low a dose. Recirculation of the chemical sludge might be an

attractive remedy.

- 2. Wrong pH. In some cases it might be necessary to adjust the pH by the addition of calcium hydroxide or sulphuric acid.
- The flocculation is insufficient. Too small flocs that are unsettleable are formed. It might be necessary to change the design of the flocculator (Jørgensen, 1979).
- P.6.18. The flocculation can be further improved by the application of synthetic polyflocculants.



Fig. 6.34. The solubility of pure metal hydroxides, as a function of pH, in water containing NTA $(10^{-4.7} \text{mol/l})$, Cl⁻ $(10^{-2.4} \text{mol/l})$ and Ca²⁺ $(10^{-2.7} \text{mol/l})$ at pH 7.0 and $10^{-2.3} \text{mil/l}$ at pH 11.0). (From Nilsson, 1971).

Clay, starch and gelatine can be used to accelerate and stimulate the flocculation, but the synthetic polyelectrolytes that have appeared on the market during the last decade or two seem to give a better efficiency (Black, 1960). They work mainly on flocs in the range of 1-50 μ m.

TABLE 6.23Synthetic organic polymeric flocculants





- B. Anionic polyelectrolytes
- 1. Polyacrylic acid



- 2. Hydrolyzed polyacrylamide: A mixture of subunits B 1 and C 1
- 3. Polystyrene sulphonate



- C. Nonionic polymers
- 1. Polyacrylamide



2. Polyethylene oxide

The long-chain polymers are able to collect many small flocs and agglomerate them into larger groups. The polymers are able to form a bridge between the small particles. For flocculation of municipal waste water anionic polyelectrolytes are chiefly used, while the cationic polyelectrolytes are used for flocculation of different types of industrial waste water or even for improving the dewatering of municipal sludge.

Several synthetic polymers are on the market, and non-ionic, anionic or cationic ones are available, see Table 6.23. For waste water treatment polyacrylamide (see below) is generally used (Robert, 1970).

Polyacrylamide

It is possible to produce polyacrylamides with a molecular weight of 4-10 million. By a copolymerization of acrylamide and acrylic acid it is possible to prepare an anionic polymer of this type.

The main effects of using polymers for flocculation are (Boeghlin, 1972 and Ericsson and Westberg, 1968):

1. Gaining a higher settling rate,

2. Reduction in turbidity, caused by small flocs.

6.3.3. Nitrification and denitrification.

P.6.19. The nitrification process eliminates oxygen consumption related to the oxidation of ammonium

$$NH_4^+ + 2O_2 - NO_3^- + H_2O + 2H^+$$
 (6.30)

As seen it is the same process as otherwise would occur in the ecosystem (see section 2.6).

Effective nitrification occurs when the age of the sludge produced by biological treatment is greater than the reciprocal rate constant of the nitrifying micro-organisms.

Bernhart (1975) has demonstrated that it is possible to oxidize ammonia in a complex organic effluent by biological nitrification.

The sludge age, f, is defined as (see also 6.2.3):

$$\frac{X}{\Delta X} = f \tag{6.31}$$

where X = the mass of biological solid in the system and ΔX = the sludge yield.

The relationship between nitrification and sludge age is shown in Fig. 6.35.



Fig. 6.35. Relationship between nitrification and sludge age.

Nitrification results from a two-step oxidation process, see 6.2.3, equations (6.5) and (6.6).

The optimum pH range for Nitrosomonas is 7.5-8.5 and for Nitrobacter 7.7-7.9. The rate seems to be dependent on the ammonium ion concentration at concentrations in excess of 0.5 mg/l, which is considerably lower than those generally found in waste water containing ammonium ions. Heavy metals are toxic at rather low concentrations. Toxic levels of about 0.2 mg/l are reported for chromium, nickel and zinc.

Temperature exerts a profound effect on nitrification (see also sections 2.4, 2.6 and Table 6.8). Downing (1966) has reported that the influence of temperature on the rate coefficient can be expressed as follows:

$$K_N = 0.18 \cdot 1.128^{T-15} (24h^{-1})$$
 (6.32)

As can be seen, $K_N = 0.18$ at 15°C. Compare with Table 6.8.

However, the amount of nitrogen which can be remoced per m^3 is limited. This is illustrated in Fig. 6.36, where it is seen that it is not possible to remove more than 21 mg/l per 24h. Even the ammonium concentration in the inflow is increased to about 1000 mg/l.



Fig. 6.36. Ammonium removal per 24h plotted against concentration.

P.6.20. Nitrate can be reduced to nitrogen and dinitrogen oxide by many of the heterotrophic bacteria present in activated sludge, but the process requires anaerobic conditions.

The pH effects the process rate, the reported optimum being above 7.0. The same process is observed in anaerobic sediment.

As the denitrifying organisms are heterotrophic, they require an organic carbon source. It is possible either to add the carbon source, e.g. by using methanol or molasses, or to use the endogenous by-product as the food supply.

If acetate is used as a carbon source the process is:

$$5CH_3COO^- + 8NO_3^- - 4N_2 + 7HCO_3^- + 3CO_3^{2-} + 4H_2O$$
 (6.33)

Fig. 6.37 illustrates the influence of the COD/NO_3^--N ratio on the denitrification efficiency. The plots shown in this figure are based on experiments for the denitrification of waste water from the manufacture of nitrogen fertilizers.



Fig. 6.37. Efficiency plotted against the ratio COD/NO3-N.



Fig. 6.38. Denitrification efficiency plotted against retention time. (1) COD removal and (2) denitrification.

The denitrification efficiency as a function of the retention time is

shown in Fig. 6.38. As seen, a minimum of 10 days retention time is required for the anaerobic denitrification process.

However, the ratio between COD and the nitrate that is removed decreases with increasing retention time (see Fig. 6.39).

The rate of denitrification increases with increasing concentrations of a available carbon and of nitrate. Francis et al. (1975) report a successful denitrification of waste water that contained more than 1000 ppm nitrate-nitrogen, which should be compared with the concentration of nitrate-nitrogen in municipal waste water of 20-40 ppm.



Fig. 6.39. Ratio COD removal per unit of time to NO₃⁻-N. Removal per unit of time plotted against retention time.

6.3.4. Stripping.

P.6.21. The stripping process is used to remove volatile gases, such as hydrogen sulphide, hydrogen cyanide and ammonia by blowing air through the waste water.

The removal of ammonia by stripping is used in the treatment of municipal waste water, but it has also been suggested for the treatment of industrial waste water or for the regeneration of the liquid used for elution of ion exchangers (Jørgensen, 1976).

P.6.22. The rate at which carbon dioxide, hydrogen sulphide, ammonia and hydrogen cyanide can be removed by air stripping is highly dependent on pH, since all four of these volatile gases are acids or bases.

Ammonia stripping is based on the following process:

 $NH_4^+ - NH_3 + H^+$

The equilibrium constant for this process is 10^{-9.25} at 18°C, which means that:

$$\frac{[NH_3][H^+]}{[NH_4^+]} = 10^{-9.25}$$

By separating H^+ in this equation and converting to a logarithmic form, we get:

$$pH = 9.25 + \log \frac{[NH_3]}{[NH_4^+]}$$
(6.34)

The same considerations are used, when the ammonium concentration is found in an aquatic ecosystem to estimate the toxicity level of the water, see section 2.4 and Table 2.13.

From equation (6.34) we can see that at pH 9.25, 50% of the total ammonia-nitrogen is in the form of ammonia and 50% in the form of ammonium. Correspondingly the ratio between ammonia and ammonium is 10 at pH 10.25 and 100 at pH 11.25. Consequently it is necessary to adjust the pH to 10 or more before the stripping process is used. Due to the very high solubility of ammonia in water a large quantity of air is required to transfer ammonia effectively from the water to the air.

The efficiency of the process depends on:

- 1. pH, in accordance with the considerations mentioned above.
- The temperature. The solubility of ammonia decreases with increasing temperature. The efficiency at three temperatures - 0°C, 20°C and 40°C - is plotted against the pH in Fig 6.40.
- 3. The quantity of air per m³ of water treated. At least 3000 m³ of air per m³ of water are required (see Fig. 6.41).
- 4. The depth of the stripping tower. The relationship between the efficiency and the quantity of air is plotted for three depths Fig. 6.41.
- 5. The specific surface of the packing (m^2/m^3) . The greater the specific surface the greater the efficiency.



Fig. 6.40. Stripping efficiency as function of pH at three different temperatures.



Fig. 6.41. Efficiency as function of m^3 of air per m^3 of water for three different depths. line = 8 m, _____ line = 6.7 m, --- line = 4 m.

Fig. 6.42 demonstrates the principle of a stripping tower. The waste

water treatment plant at Lake Tahoe, California, includes a stripping process. $10,000 \text{ m}^3$ of waste water is treated per 24h at a cost of approximately 3 US cents per m³. The investment cost is in the order of 5 US cents per m³ (based on 16% depreciation and interest per year of the investment).



Fig. 6.42. The principle of a stripping tower.

The cost of stripping is relatively small, but the process has two crucial limitations:

- 1. It is practically impossible to work at temperatures below 5-7°C. The large quantity of air will cause considerable evaporation, which means that the water in the tower is freezing.
- 2. Deposition of calcium carbonate can reduce the efficiency or even block the tower.

Due to limitation 1) it will be necessary to use warm air for the

stripping during winter in temperate climates, or to instal the tower indoors. This makes the process too costly for plants in areas with above 10,000 inhabitants and limits the application for treatment of bigger volumes to tropical or maybe subtropical latitudes.

However, it seems advantageous to combine the process with ion exchange. By ion exchange it it possible to transfer ammonium from 100 m^3 of waste water to 1 m^3 of elution liquid. As elution liquid is used as a base (see 6.3.6), a pH adjustment is not required. Furthermore, the ratio of air to water is not increased although the elution liquid has a 100 times greater ammonia concentration. Consequently a stripping tower 100 times smaller with a preconcentration by ion exchange can be used.

Recovery of ammonia, for use as a fertilizer, also seems easier after the preconcentration. The stripped ammonia could, for example, easily be absorbed into a sulphuric acid solution, for the production of ammonia sulphate.

As mentioned in the introduction, the shortcoming of some of the technological solutions is, that they do not consider a total environmental solution, as they solve one problem but create a new one. The stripping process is a characteristic example, since the ammonia is removed from the waste water but transferred to the atmosphere, unless recovery of ammonia is carried out. In each specific case it is necessary to assess whether the air pollution problem created is greater that the water pollution problem solved.

6.3.5. Chlorination and adsorption on activated carbon.

P.6.23. Chlorine can oxidize ammonia in accordance with the following reaction sheme:

 $Cl_{2} + H_{2}O + HOCI + HCI$ $NH_{3} + HOCI + NH_{2}CI + H_{2}O$ $NH_{2}CI + HOCI + NHCI_{2} + H_{2}O$ $NHCI_{2} + HOCI + NCI_{3} + H_{2}O$ (6.35)

Activated carbon is able to adsorb chloramines, and so a combination of chlorination and adsorption on activated carbon can be applied for removal of ammonia.

The most likely reaction for chloramine on activated carbon is:

$$C + 2NHCl_2 + H_2O - N_2 + 4H^+ + 4Cl^- + CO$$
 (6.36)

Further study is needed, however, to show conclusively that surface oxidation results from this reaction. Furthermore, it is important to know that the Cl_2/NH_3 -N oxidized mole ratio is 2:1, which is required for ammonium oxidation by this pathway.

The monochloramine reaction with carbon appears more complex. On fresh carbon the reactio is most probably:

$$NH_{2}CI + H_{2}O + C + NH_{3} + H^{+} + CI^{-} + CO$$
 (6.37)

After this reaction has proceeded to a certain extent, partial oxidation of monochloramine is observed, possibly according to the reaction:

$$2NH_{g}CI + CO + N_{g} + H_{g}O + 2H^{+} + 2CI^{-} + C$$
 (6.38)

It has been observed that acclimation of fresh carbon is necessary before monochloramine can be oxidized.

In the removal of ammonia with a dose of chlorine followed by contact with activated carbon, pH control can be used to determine the major chlorine species. The studies reported herein indicate that a pH value near 4.5 should be avoided, because $\rm NHCl_2$ predominates and thus 10 parts by weight of chlorine are required for each part of $\rm NH_3$ -N oxidized to N₂. At a slightly higher pH and acclimated carbon, the portion of monochloramine increases and the chlorine required per unit weight of $\rm NH_3$ -N oxidized should approach 7.6 parts, ignoring the chlorine demand resulting from other substances. However, further testing should be used to verify this conclusion in each individual case.

When accidental overdosing of chlorine has occurred or after an intentional addition of large quantities of chlorine to accelerate disinfection, it will be desirable to remove the excess chlorine. This is possible using a reducing agent, such as sulphur dioxide, sodium hydrogen sulphite or sodium thiosulphate.

Complete removal of the 25-40 mg per litre ammonium-N is far too costly by this method. Chlorine costs about 25-30 US cents per kg, which means that the chlorine consumption alone will cost about 6 US cents per m^3 waste. When the capital cost and the other operational costs are added the total treatment cost will be as high as 13-17 US cents per m^3 , which is considerably more expensive than other removal methods.

It is possible to use chlorine to oxidize ammonium compounds to free nitrogen, but this process involves even higher chlorine consumption and, therefore, is even more expensive.



Fig. 6.43. Waste water treatment plant Pretoria. After mechanicalbiological treatment: 2) aeration, 3) lime precipitation, 4) sludge drying, 5) ammonia stripping, 6) recarbonization, 7) sand filtration, 8) chlorination, 9) adsorption on activated carbon, 10) chlorination.

The method has, however, one advantage: by using sufficient chlorine it is possible to obtain a very high efficiency. This has meant that the method has found application after other ammonium removal methods, where high efficiencies are required. This is the case when the waste water is reclaimed, for example in the two plants shown in Figs. 6.43 and 6.44. As seen it is necessary to use several treatment processes to achieve a sufficient water quality after the treatment. Chlorination and treatment on activated carbon are used as the last treatment to assure good ammonium removal and sufficient disinfection of the water. An additional chlorination is even used after the treatment on activated carbon to ensure a chlorine residue in the water supply system.



Fig. 6.44. Production of potable water from waste water (Windhoek).

- 6.3.6. Application of ion exchange for removal of nutrients.
- P.6.24. Ion exchange is a process in which ions on the surface of the solid are exchanged for ions of a similar charge in a solution with which the solid is in contact. Ion exchange can be used to remove undesirable ions from waste water. Cations (positive ions) are exchanged for hydrogen or sodium and anions (negative ions) for hydroxide or chloride ions.

The cation exchange on a hydrogen cycle can be illustrated by the following reaction, using, in this example, the removal of calcium ions, which are one of the ions (Ca^{2+} and Mg^{2+}) that cause hardness of water:

 $H_2R + Ca^{2+} - CaR + 2H^+$ (6.39)

where R represents the resin.

The anion exchange can be similar illustrated by the following reactions:

$$SO_4^{2-} + R(OH)_2 \Rightarrow SO_4R + 2OH^-$$
 (6.40)

When all the exchange sites have been replaced with calcium or sulphate ions, the resin must be regenerated. The cation exchanger *can* be regenerated by passing a concentrated solution of sodium chloride through the bed, while the anion exchanger, which in this case is of hydroxide form, must be treated by a solution of hydroxide ions, e.g. sodium hydroxide.

lon exchange is known to occur with a number of natural solids, such as soil, humus, metallic minerals and clay, see also section 4.9. *Clay*, and in some instances other natural materials, can be used for demineralization of drinking water. In the context of adsorption, the ability of aluminium oxide to make a surface ion exchange should be mentioned, but the natural clay mineral, *clinoptilolite*, can also be used for waste water treatment as it has a high selectivity for removal of ammonium ions.

Synthetic ion exchange resins consist of a network of compounds of high molecular weight to which ionic functional groups are attached. The molecules are cross-linked in a three-dimensional matrix and the degree of the cross-linking determines the internal pore structure of the resin. Since ions must diffuse into and out of the resin, ions larger than a given size may be excluded from the interaction through a selection dependent upon the degree of cross-linking. However, the nature of the groups attached to the matrix also determines the ion selectivity and thereby the equilibrium constant for the ion exchange process.

The cation exchangers contain functional groups such as *sulphonic* $R-SO_3-H$ -*carboxylic*, R-COOH-*phenolic*, R-OH and *phosphonic*, $R-PO_3H_2$ (R represents the matrix). It is possible to distinguish between strongly acidic cation exchangers derived from a strong acid, such as H_2SO_4 , and weakly acidic ones derived from a weak acid, such as H_2CO_3 . It is also possible to determine a pK-value for the cation exchangers in the same way as it is for acide generally.

This means:

 $R-SO_3H + R-SO_3^+ + H^+$

$$\frac{[H^+] * [R-SO_3^-]}{[R-SO_3H]} = K \quad pK = -\log K \quad (6.41)$$

Anion exchange resins contain such functional groups as *primary amine*, R-NH₂, *secondary amine*, R-R₁NH, and *tertiary amine* R-R₁-R₂N groups and the *quaternary ammonium group* R-R₁R₂R₃N⁺OH⁻.

It can be seen that the anion exchanger can be divided into weakly basic and strongly basic ion exchangers derived from quaternary ammonium compounds.

It is also possible to introduce ionic groups onto natural material. This is done using cellulose as a matrix, and due to the high porosity of this material it is possible to remove even high molecular weight ions.

Preparation of cation exchange resin, using hydrocarbon molecules as a matrix, is carried out by polymerization of such organic molecules as styrene and metacrylic acid.

The degree of cross-linking is determined by the amount of divinylbenzene added to the polymerization. This can be illustrated by the example shown below.



P.6.25. It is characteristic that the exchange occurs on an
equivalent basis. The capacity of the ion exchanger is usually expressed as equivalent per litre of bed volume.

When the ion exchange process is used for reduction of hardness, the capacity can also be expressed as kg of calcium carbonat per m^3 of bed volume. Since the exchange occurs on an equivalent basis, the capacity can be found based either on the number of ions removed or the number of ions released. Also, the quantity of regenerant required can be calculated from the capacity. However, neither the resin nor the regeneration process can be utilized with 100% efficiency.

The Fig. 6.45 plot is often used as an illustration of the preference of an ion exchange resin for a particular ion. As seen, the percentage in the resin is plotted against the percentage in solution.



Fig. 6.45. Illustration of the preference of an ion exchange resin for a particular ion.

The selectivity coefficient, K_{AB} , is not actually constant, but is dependent upon experimental conditions. A selectivity coefficient of 50% in solution is often used = ${}^{a}_{50\%}$.

If we use concentration and not activity, it will involve, for monocharged ions:

$$C_{B} = C_{A}$$

 $a_{50\%} = K_{AB,50\%} = \frac{C_{RA}}{C_{RB}}$ (6.42)

The plot in Fig. 6.45 can be used to read a 50%.

The selectivity of the resin for the exchange of ions is dependent upon the ionic charge and the ionic size. An ion exchange resin generally prefers counter ions of high valence. Thus, for a series of typical anions of interest in waste water treatment one would expect the following order of selectivity:

 $PO_4^{3-} > SO_4^{2-} > CI^-$.

Similar for a series of cations:

 $AL^{3+} > Ca^{2+} > Na^{+}$.

But this is under circumstances where the internal pore structure of the resin does not exclude the ions mentioned from reaction. Organic ions are often too large to penetrate the matrix of an ion exchange, which is, of course, more pronounced when the resins considered have a high degree of cross-linking. As most kinds of water and waste water contain several types of ions besides those which must be removed it is naturally a great advantage to have a resin with a high selectivity for the ions to be removed during the ion exchange process.

The resin utilization is defined as the ratio of the quantity of ions removed during the actual treatment to the total quantity of ions that could be removed at 100% efficiency; this is the theoretical capacity. The regeneration effeciency is the quantity of ions removed from the resins compared to the quantity of ions present in the volume of the regererant used.

Weak base resin has a significant potential for removing certain organic compounds from water, but the efficiency is highly dependent upon the pH.

It seems reasonable to hypothesize that an adsorption is taking place by the formation of a hydrogen bond between the free amino groups of the resin and hydroxyl groups of the organic substance taken up. As pH decreases, so that the amino groups are converted to their acidic form, the adsorption capacity significantly decreases.

The exchange reaction between ions in solution and ions attached to the resin matrix is generally reversible. The exchange can be treated as a simple stoichiometric reaction. For cation exchange the equation is:

$$A^{n+} + n(R^{-})B^{+} + nB^{+} + (R^{-})_{n}A^{n+}$$
 (6.43)

The ion exchange reaction is selective, so that the ions attached to the fixed resin matrix will have preference for one counter ion over another. Therefore the concentration of different counter ions in the resin will be different from the corresponding concentration ration in the solution.

According to the law of mass action, the equilibrium relationship for reaction (6.43) will give:

$$K_{AB} = \frac{a_{B}^{n} * a_{RA}}{a_{A} * a_{RB}^{n}}$$
(6.44)

where a_B and a_A are the activity of the ions B⁺ and Aⁿ⁺ in the solution and correspondingly a_{RB} and a_{RA} are the activities of the resin in B- and A-form, respectively.

As mentioned above the clay mineral, clinoptilolite, can take up ammonium ions with a high selectivity. This process is used for the removal of ammonium from municipal waste water in the U.S.A., where good quality clinoptilolite occurs.

Clinoptilolite has less capacity than the synthetic ion exchanger, but its high selectivity for ammonium justifies its use for ammonium removal. The best quality clinoptilolite has a capacity of 1 eqv. or slightly more per litre. This means that 1 litre of ion exchange material can remove 14 g ammonium -N from waste water, provided all the capacity is occupied by ammonium ions. Municipal waste water contains approximately 28 g (2 eqv.) per m^3 , which means that 1 m^3 of ion exchange material can treat 500 m^3 waste water (which represents a capacity of 500 bed volumes). The practical capacity is, however, considerably less - 150-250 bed volumes - due to the presence of other ions that are taken up by the ion exchange material, although the selectivity is higher for ammonium that for the other ions present in the waste water. The concentration of sodium, potassium and calcium ions might be several eqv. per litre, compared with only 2 eqv. per litre of ammonium ions.

Clinoptilolite is less resistant to acids or bases than synthetic ion exchangers. A good elution is obtained by the use of sodium hydroxide, but as the material is dissolved by sodium hydroxide a very diluted solution should be used for elution to minimize the loss of material. A mixture of sodium chloride and lime is also suggested as alternative elution solution.

The flow rate through the ion exchange column is generally smaller for clinoptilolite than for synthetic material resin - 10 m as against 20-25 m.

The elution liquid can be recovered, as mentioned in 6.3.4, by air

stripping. The preconcentration on the ion exchanger makes this process attractive - the sludge problem is diminished and the cost of chemicals reduced considerably. For further details about this method of recovery, see Jørgensen (1975).

Phosphate can also be removed by an ion exchange process. Synthetic ion exchange material can be used, but due to the presence of several eqv. of anions, it seems a better solution to use activated aluminium, which is a selective adsorbant (ion exchanger) for phosphate.

In accordance with Neufeld and Thodos (1969) the phosphorus adsorption on aluminia is a dual process of ion exchange and chemical reaction, although many authors refer to the process as an adsorption.



Fig. 6.46. Flowchart of a combination of chemical precipitation and ion exchange. (A) a submersible pump, (B) the settling basin, (C) an intermediate vessel, where carbon dioxide is added, (D) a carbon dioxide bomb (50 atm., 25 lit.), (E) a pump feeding the ion exchangers, (F) elution liquid, (G) a handpump, (H) a dosing pump.

The selectivity for phosphorus uptake is very high (Yee, 1960), and only a minor disturbance from other ions is observed. Municipal waste water contains about 10 mg phosphorus or 1/3 eqv. P per 1 m³. If the aluminia is

activated by nitric acid before use, the theoretical capacity will be as high as 0.561 eqv. per litre or 1500-3000 bed volumes. The practical capacity is lower - about 1000 bed volumes (Ames, 1969).

Also activated aluminia can be regenerated by sodium hydroxide, but again the use of a low concentration is recommended to reduce loss of material (Ames, 1970). Aluminia has a high removal efficiency for all inorganic phosphorus species in waste water, but removal efficiency for organic phosphorus compounds is somewhat lower. Jørgensen (1978) has suggested the use of an anionic cellulose exchanger together with activated aluminia as a mixed bed ion exchange column to improve the overall efficiency for removal of all phosphorus species present in waste water, including the organic ones.

A combination of chemical precipitation and ion exchange has developed as an alternative to the mechanical-biological-chemical treatment method. A flowchart of such a plant is shown in Fig. 6.46.

After the chemical precipitation the waste water is treated on two ion exchangers (which, however, could be in one mixed bed column). The first ion exchanger is cellulose based for removing proteins and reducing BOD_5 . The second column could be either clinoptilolite or activated aluminia + the above mentioned cellulose anion exchanger. A plant using this process has been in operation since 1973 in Sweden, giving results comparable with or even better than the generally applied 3 steps treatment (see Table 6.24). The capital cost and operational costs are approximately the same as for a 3 steps plant. However, the plant produces 2-4 times less sludge than the normal 3 step plant, giving a correspondingly lower sludge treatment cost.

TABLE 6.24

Analysis of municipal waste water after chemical precipitation + ion exchange (mg l⁻¹) (flowchart see Fig. 6.46)

BOD ₅ COD	10 - 18 30 - 45 < 01
N	10 - 20

6.3.7. Algal ponds.

P.6.26. The uptake of nutrients by algae can be utilized as a waste water treatment process. Per 100 g of dry matter phytoplankton will, on average, contain 4-10 g nitrogen and 0.5-2.5 g phosphorus.

The process is known from the entrophication problem, see section 2.7. It

can be considered a biological nutrient removal.

Algal ponds will, under favourable conditions be able to produce 100 g phytoplankton per m^3 during 24 hours, which means that as much as 25% of the nitrogen and phosphorus can be removed from solution into phytoplankton (i.e. into suspension) during 24 hours. It a retention time of 3-5 days is applied, as much as 40-60% of the nutrient in municipal waste water will be removed from solution.

If a chemical precipitation follows the treatment in algal ponds the suspended phytoplankton can easily be removed.

The cost of the method is moderate, and the removal of nitrogen especially is often a great advantage. The method is used in the plant in Windhoek (see Fig. 6.44) prior to the chemical precipitation with aluminium sulphate.

The method has, however, some pronounced disadvantages that limit its applications:

- 1. Only in tropical or subtropical regions is solar radiation sufficient throughout the year to ensure an acceptable efficiency.
- 2. The areas needed are large 3-5 days retention time.
- 3. The growth of phytoplankton is *sensitive to many organic compounds*, e.g. mineral oil.

Another biological nutrient-removal method should be mentioned in this context: **a root-zone plant**. This has been discussed only recently in Europe, but quite a wide range of results from various studies has been published. More than 90% removal of P and N with 2 m^2 root zone area per pers. equiv. has been quoted, but other studies refer to removal efficiencies under same conditions of less than 10%. Further studies are needed before general conclusions can be drawn.

The dimension of a root-zone plant can be found from the following equation:

 $\log (C/C_o) = -A_i V/Q$

(6.45)

where

C is the concentration in the treated water (e.g. as BOD₅ mg/l),

C_o is the concentration in the inflow.

Ai is a constant (found in several experiments to be about 0.13 l/24h)

V is the plant volume (m³) and

Q is the flowrate (m³/24h)

The dimensions should also account for the soil permeability. The flow, Q_m , which can pass through soil is

 $Q_m = b + d + K_o + i$

(6.46)

where

b is the width of the plant d the depth of the plant K_o the soil permeability (m/24h) and i is the slope (m/m)

d is usually in the order of 0.5-1.0 m and since $V = I \bullet b \bullet d$, where I is the length of the plant, b and I are selected in such a way that $Q_m > Q$. Often Q_m is chosen to be 3-4 times Q to account for precipitation. For further details on this promising method, see Boyt et al. (1977); Reddy et al. (1982); Bucksteeg et al. and Finlayson and Chic (1983).

6.4. REMOVAL OF TOXIC ORGANIC COMPOUNDS.

6.4.1. The problem and source of toxic organic compounds.

The presence of toxic organic compounds in waste water is causing severe problems:

- 1. Since toxic organics are scarcely decomposed in the biological plant, life in the receiving water will suffer from their toxic effect. The fate of toxic substances in aquatic ecosystems is already covered in sections 2.13, 5.2 and 5.4.
- 2. Inhibition of the biological treatment might reduce the efficiency of this process considerably.

Here the inhibition of biological treatment will be considered in more detail, in relation to heavy metals as well as toxic organic compounds.

P.6.27. The biological reactions are influenced by the presence of inhibitors. In the case of competitive inhibition, the Michaelis-Menten equation (see 6.2.3) becomes:

$$\mu = \mu_{m} \frac{S}{S + K_{s} + (K_{s,1} + 1)/K_{s,1}}$$
(6.47)

where $K_{S,I}$ = inhibition constant, and I = concentration of the inhibitor(s).

Competitive inhibition occurs when the inhibitor molecule has almost the same structure as the substrate molecule, which means that the micro-organism is able to break down the inhibitor and the substrate by the same, or almost the same, biochemical pathway. The resulting influence on the Lineweaver-Burk plot (equation 6.12 in 6.2.3) is also shown in Fig. 6.47.



Fig. 6.47. Lineweaver-Burk plot (1). (2) the plot when a toxic compound is present. (3) the plot when a competitive inhibition takes place.

P.6.28. If a toxic compound (non-competitive inhibitor) is present, only the maximum growth rate will be influenced, and it is reduced according to the relationship:

$$\mu_{m}^{+} = \mu_{m}^{+} - \frac{K_{s,i}}{K_{s,i} + \Gamma}$$
(6.48)

In this case the Lineweaver-Burk plot is also changed (see Fig. 6.47). Heavy metals and cyanide are examples of toxic materials that inhibit non-competitively. The approximate values of $K_{s,1}$ for some inhibitors are given in Table 6.25.

Uptake of toxic substances (organic compounds as well as heavy metals) by the biomass depends on several factors, including pH and the concentration of organic matter and metals present in the system. A higher initial concentration of the toxic substance or sludge increases the overall uptake. In general, the uptake capacity increases with increasing pH. Although the affinity of the biomass for the toxic substances is relatively small, it is generally higher than that of competing organics in a supernatant. The largescale accumulation of some toxic substances by activated sludge with its subsequent removal in a secondary clarifier explains the significant reduction observed in many treatment plants.

TABLE 6.25 Effect of inhibitors

Non-competitive K _{S,I} (mg/I) nhibitor		
Hg Ag Co Cu Ni Cr ⁶⁺ CN ⁻	2 5 10 20 40 200 200-2000	

In general industrial waste water contains toxic organics, which consequently **must be removed** before this waste water is discharged into the municipal sewage system. Only in this way can the two problems mentioned above be solved simultaneously.

Compounds of minor toxicity and with a biodegradation rate slightly slower than average for municipal waste water can be tolerated in municipal waste water at low concentrations. However, industrial waste water containing medium or high levels of toxic compounds should not be discharged into the municipal sewage system without effective treatment.

As a first estimation of the relationship between the composition of an organic compound and its biodegradability, the following rough rules can be used:

- 1. **Polymer compounds** are generally *less biodegradable* than monomer compounds.
- 2. Aliphatic compounds are *more biodegradable than* **aromatic com- pounds.**
- 3. **Substitutions**, especially with *halogens and nitro groups*, will *de-crease* the biodegradability.
- 4. Introduction of **double bonds** will generally mean *an increase in the biodegradability*.
- 5. Introduction of an **oxygen bridge** -O- or a **nitrogen bridge** -N- in an molecule will *decrease the biodegradability*.
- 6. **Tertiary or secondary compounds** (defined as compounds that contain tertiary or secondary carbon atoms) *are less biodegradable* than the corresponding primary compounds.

Many solvents, for instance alcohol (C2H5OH) and acetone (CH3COCH3),

have a biodegradability similar to that of municipal waste water, but still they should not be discharged into the municipal sewer except in very small amounts as they have a high oxygen consumption. As seen from:

$$C_2H_5OH + 3O_2 - 2CO_2 + 3H_2O$$
 (6.49)

100 kg 24 hr⁻¹ of ethanol has an oxygen consumption of 209 kg 24 hr⁻¹ corresponding to approximately 4175 inhabitants (1 person eqv. to 50 g BOD_5 24 hr⁻¹).

TABLE 6.26

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Biodegradable organic compounds	Non-biodegradable organic compounds		
Aliphatic acids	Ethers		
Aliphatic alcohols	Ethylene chlorine hydrine		
Aliphatic primary and secondary alcohols	Isoprene		
Aliphatic aldehydes	Butadiene		
Aliphatic esters	Methylvinyl keton		
Alkvibenzene sulphonates	Naphtalene		
Amines	Various polymeric compounds		
Mono- and dichlorophenols	Polypropylene benzene sulphonates		
Glycols	Certain carbon hydrides, especially of aromatic struc- tures, including alkyl-aryl compounds		
Nitriles	Tertiary benzene sulphonate		
Phenois	Tri-, tetra- and pentachlorophenols		
Styrene	· · ·		
Phenyi acetate			

A survey of biodegradable and non-biodegradable organic compounds is given in Table 6.26 (Ludsack and Ettinger, 1960).

Apart from biological treatment with acclimated sludge, which is applicable in some cases, the following methods might come into consideration for treatment of toxic organics:

- 1. Separators for removal of oil.
- 2. Flocculation. With flocculation it is possible to remove a wide range of organic colloids.
- 3. Extraction. This method is generally rather costly, but recovery of chemicals will often justify the high cost. The method is mostly used when high concentrations are present in the waste water.
- 4. Flotation is of special interest when impurities with a specific gravity of less than 1 are present in the waste water.
- 5. Adsorption. A wide range of organic compounds, such as insecticides and dyestuffs can be adsorbed by activated carbon.
- 6. Sedimentation is only used in conjunction with removal of suspended matter or in combination with a chemical precipitation or flocculation

and biological treatment.

- Oxidation and reduction are mainly used for the treatment of cyanides, some toxic dyestuffs and chromate. The process might be rather costly.
- 8. Distillation of waste water is used when the recovery of solvents is possible or when other methods are not available; for the treatment of radioactive waste water, for example. The method is very costly.
- 9. Organic acids and bases can be removed by ion exchange.
- 10. Filtration can be used for the removal of suspended matter from small quantities of waste water.
- 11. Neutralization. In all circumstances it is necessary to discharge the waste water with a pH between 6 and 8. Calcium hydroxide, sulphuric acid and carbon dioxide are used for the neutralization process.

In the following paragraphs, process numbers 2, 5 and 7 will be discussed in more detail, as they are the most important processes for treatment of industrial waste water containing toxic organics.

6.4.2. Application of chemical precipitation for treatment of industrial waste water.

Chemical precipitation for the removal of phosphorus compounds has been mentioned in 6.3.2. At the same time as it precipitates phosphorus compounds, the process will reduce the BOD_5 by approximately 50-70%. This effect is mainly a result of adsorption on the flocs formed by the chemical precipitation. As this is a chemico-physical effect it is understandable that the COD is also reduced by 50-70%, while the biological treatment will always show a smaller effect on COD removal than on BOD_5 reduction.

The chemical precipitation used for municipal waste water - precipitation with aluminium sulphate, iron(III)chloride and calcium hydroxide - is therefore also able to remove many organic compounds, toxic as well as non-toxic, which means that the process is applicable for the treatment of some types of industrial waste water.

In addition to these three precipitants

P.6.29. a wide range of chemicals is used for the precipitation of industrial waste water: hydrogen sulphide, xanthates, sodium hydroxide, bentonite, kaoline, starch, polyacrylamide, lignin sulphonic acid, dodecylbenzensulphonic acid, glucose trisulphate.

Table 6.27 gives a survey, with references, of the use of chemical

precipitation for different types of industrial waste water.

TABLE 6.27

Use of chemical precipitation for treatment of industrial waste water

Type of waste water	Chemical used	Reference
Metal plating and finishing industry	Lime	Schjødtz-Hansen, 1968
Iron industry and mining	Lime, Aluminium sulphate	S.E. Jørgensen, 1973
Electrolytic industry	Hydrogen sulphide	S.E. Jørgensen, 1973
Coke and tar industry	Lime or sodium hydroxide	S.E. Jørgensen, 1973
Cadmium mining	Xanthates	Hasebe & Yamamoto, 1970
Manufacturing of glass- and stone wool	Sodium hydroxide	Schjødtz-Hansen & Krogh, 1968
Oil refineries	Aluminium sulphate, iron(III) chloride	S.E. Jørgensen, 1973
Manufacture of organic chemicals	Aluminium sulphate, iron(III) chloride	S.E. Jørgensen, 1973
Photochemicals	Aluminium sulphate	S.E. Jørgensen, 1973
Dye industry	Iron(II) salts, aluminium sulphate, lime	S.E. Jørgensen, 1973
Fertilizer industry	PO ₄ ³⁻ : Iron(II) salts, aluminium	S.E. Jørgensen, 1973
	sulphate, lime, NH ₄ ⁺ : magnesium	
	sulphate + phosphate	
Plastics industry	Lime	S.E. Jørgensen, 1973
Food industry	Lignin sulphonic acid, dodecylbenzen- sulphonic acid, glucose trisulphate, iron(III) chloride, aluminium sulphate	S.E. Jørgensen, 1973
Paper industry	Bentonite, kaoline, starch, polyacrylamide	S.E. Jørgensen, 1973
Textile industry	Bentonite, aluminium sulphate	S.E. Jørgensen, 1973

6.4.3. Application of adsorption for treatment of industrial waste water.

P.6.30. Adsorption involves accumulation of substances at an interface, which can either be liquid-liquid, gas-liquid, gas-solid or liquid-solid. The material being adsorbed is termed the adsorbate and the adsorbing phase the adsorbent.

The word sorption, which includes both adsorption and absorption, is generally used for a process where the components move from one phase to another, but particularly in this context when the second phase is solid.

A solid surface in contact with a solution has the tendency to accumulate a surface layer of solute molecules, because of the imbalance of surface forces, and so an adsorption takes place. The adsorption results in the formation of a molecular layer of the adsorbate on the surface. Often an equilibrium concentration is rapidly formed at the surface and is generally followed by a slow diffusion onto the particles of the adsorbent.

P.6.31. The rate of adsorption is generally controlled by the rate of diffusion of the solute molecules. The rate varies reciprocally with the square of the diameter of the particles and increases with increasing temperature (Weber and Morris, 1963). For practical application either Freundlich's isotherm or Langmuir's isotherm provide a satisfactory relationship between the concentration of the solute and the amount of adsorbed material.

The Freundlich isotherm is expressed in the following equation (compare with equation (6.28)):

$$\mathbf{\dot{a}} = \mathbf{k} \mathbf{\dot{c}}^{\mathsf{n}} \tag{6.50}$$

where

k and n = constants

a = the amount of solute adsorbed per unit weight

C = the equilibrium concentration of the solute in the liquid phase

The values of k and n are given for several organic compounds in Table 6.28 (Rizzo and Shepherd, 1977).

TABLE 6.28 Freundlich's constant for adsorption of some organic compounds on activated carbon

Compound	k	n	
Aniline Benzene sulphonic acid Benzoic acid Butyraldehyde Butyric acid Chiorobenzene Ethylacetate Methyl ethyl ketone Nitrobenzene Phenol Phenol	к 25 7 4.4 3.3 3.1 40 0.6 24 82 24 24 24	n 0.322 0.169 0.237 0.445 0.570 0.533 0.406 0.833 0.406 0.833 0.183 0.237 0.271 0.271	
Toluene Vinyl chloride	30 0.37	0.729 1.088	

*) a in mg/g when C in mg/l

Langmuir's adsorption isotherm is based on the following expression:

$$a = \frac{A_{o} * C}{1 + b * C}$$
(6.51)

where

a and C = as defined above b and A_{o} = constants

As can be seen, $a = A_0/b$ when $C = \infty$.

Adsorption of nutrients, heavy metals and organics in sediment and soil is in principle the same process, see also section 4.10.

TABLE 6.29 Langmuir's constant for adsorption of some organic compounds on activated carbon

Compound	A _o	b (l/mg)
Phenol	0.118	1.15
p-Nitrochloro-benzene	0.286	0.714
Dodecylbenzene sulphonate	1.83	13.2

*) a in mg/l when C in mg/l

The Langmuir constant for several organic compounds that can be adsorbed on activated carbon has been found by Weber and Morris (1964). Most types of waste water contain several substances that will be adsorbed, and in this case a direct application of Langmuir's adsorption isotherm is not possible.

Weber and Morris (1965) have developed an equation (6.52) and (6.53) for competitive adsorption of two substances (A and B). In other words, competitive adsorption can be described in the same way as a competitive enzymatic reaction:

$$a_{A} = \frac{A_{Ao} * C_{A}}{1 + b_{A} * C_{A} + b_{B} * C_{B}}$$
(6.52)

$$a_{B} = \frac{A_{Bo} \circ C_{B}}{1 + b_{A} \circ C_{A} + b_{B} \circ C_{B}}$$
(6.53)

Langmuir's constant for some organic compounds generally found in waste water are shown in Table 6.29.

When it is necessary to find whether Freundlich's adsorption isotherm or

Langmuir's adsorption isotherm gives the best fit to a set of data, the two plots in Figs. 6.48 and 6.49 should be used.



Fig. 6.48. Adsorption of lysine on a cellulose cation exchanger at three different pH values. (Jørgensen, 1976).

When a linear relationship between log a and log C is obtained, Freundlich's adsorption isotherm is a good description of a set of dats, as:

 $\log a = \log k + n \log C$

(6.54)

When the reciprocal values of a and C give a linear equation (see Fig. 6.49) Langmuir's adsorption isotherm, equation (6.51), gives a good description of the set of data, since

$$\frac{1}{a} = \frac{1 + b + C}{A_0 + C}$$
or
$$\frac{1}{a} = \frac{1}{A_0} + \frac{1}{C} + \frac{b}{A_0}$$

Notice that Fig. 6.49, is a parallel to Lineweaver-Burk's plot used for enzymatic processes, see also Fig. 6.47.



Fig. 6.49. Adsorption of uric acid on activated carbon (pH = 9.0. Jørgensen, 1976).

It is possible, to a certain extent, to predict the adsorption ability of a given component. The solubility of the dissolved substance is by far the most significant factor in determining the intensity of the driving forces.

P.6.32. The greater the affinity of a substance for the solvent, the less likely it is to move towards an interface to be adsorbed. For an aqueous solution this means that the more hydrophilic the substance is, the less likely it is to be adsorbed. Conversely, hydrophobic substances will be readily adsorbed from aqueous solutions.

Many organic components, e.g. sulphonated alicylic benzenes, have a molecular structure consisting of both hydrophilic and hydrophobic groups. The hydrophobic parts will be adsorbed at the surface and the hydrophilic parts will tend to stay in the water phase.

The sequential operation is frequently called "contact filtration", because the typical application includes treatment in a mixing tank followed by filtration, but more frequently settling is used for removal of the used adsorbents in industrial waste water engineering. The sequential adsorption operation is limited to treatment of solutions where the solute to be removed is adsorbed relatively strongly when compared with the remainder of the solution. This is often the case when colloidal substances are removed from aqueous solutions using carbon, as in the production of process water.

The method for dealing with the spent adsorbent depends upon the system under consideration. If the adsorbate is valuable material, it might

be desorbed by contact with a solvent other than water. If the adsorbate is volatile, it may be desorbed by reduction of the partial pressure of the adsorbate over the solid by passing stram or air over the solid. In the case of most sequential adsorption operations in the context of waste water treatment, the adsorbate is of no value and it is not easily desorbed. The adsorbent may then be regenerated by burning off the adsorbate, followed by reactivation.

In the continuous operation, the water and the adsorbent are in contact throughout the entire process without a periodic separation of the two phases. The operation can either be carried out in strictly continuous steady-state fashion by movement of the solid as well as the fluid, or in a semicontinuous fashion characterized by moving fluid but stationary solid, the so-called fixed adsorption.

Due to the inconvenience and relatively high cost of continuously transporting solid particles, it is generally found more economical to use a stationary bed of adsorbent for waste water treatments.

The design of a fixed bed adsorber and the prediction of the length of adsorption cycle requires knowledge of the percentage approach to saturation at the break point. Fig. 6.50 shows an idealized breakthrough curve.

P.6.33. The extent of adsorption is proportional to the surface area.



Fig. 6.50. Idealized breakthrough curve. Concentration (Y) versus volume (W)

In order to compare different adsorbents a specific surface area, defined as that portion of the total surface area that is available for adsorption per unit of adsorbent, is used. This means that the adsorption capacity of a non-porous adsorbent should vary inversely with the particle diameter, while in the case of highly porous adsorbent, the capacity should be almost independent of the particle diameter. However, for some porous material, such as activated carbon, the breaking up of large particles to form smaller ones opens some tiny sealed channels in the column, which might the become available for adsorption (Weber and Morris, 1964).

The nature of the adsorbate also influences the adsorption. In general an inverse relationship can be anticipated between the extent of adsorption of a solute and its solubility in the solvent (water) from which adsorption occurs. This is the so-called Lundilius' rule, which may be used for semiquantitative prediction of the effect of the chemical character of the solute on its uptake from solution (water) (Lundilius, 1920).

P.6.34. Ordinarily, the solubility of any organic compound in water decreases with increasing chain length because the compound becomes more hydrophobic as the number of carbon atoms increases. This is Traube's rule.

Adsorption from aqueous solution *increases as homologous series are ascended*, largely because the expulsion of increasingly large hydrophobic molecules from water permits an increasing number of water-water bonds to form. Fig. 6.51 shows the effect of molecular weight on the capacity for adsorption for several sulphonated alkylbenzenes. As seen, the figure illustrates very well the above-mentioned Traube's rule. The molecular weight is also related to the rate of uptake of solutes by activated carbon, if the rate is controlled by intraparticle transport. Data are plotted in Fig. 6.52 for the rates of adsorption of a series of sulphonated alkylbenzenes of different molecular size. It can be seen that the molar rate of uptake decreases with increasing molecular weight.

pH strongly influences the adsorption as hydrogen and hydroxide ions are adsorbed, and the charges of the other ions are influenced by the pH of the water. For typical organic pollutants from industrial waste water, the adsorption increases with increasing pH.

Normally, the adsorption reactions are exothermic, which means that the adsorption will increase with decreasing temperature, although small variations in temperature do not tend to alter the adsorption process to a significant extent.

P.6.35. Adsorption can be used to remove several organic compounds, such as phenol, alkylbenzene-sulphonic-acid,

dyestuffs and aromatic compounds from waste water by the use of activated carbon.



Fig. 6.51. Effect of molecular weight on capacity for adsorption for several sulphonated alkylbenzenes.





Scaramelli et al. (1973) have examined the effect (on effluent quality) of adding powdered activated carbon to an activated sludge system.

They found that 100 to 200 mg/l were able to reduce TOC from about 20 mg/l to 7 mg/l.

Activated carbon has also been suggested as an adsorbent for the removal of refractory dyestuffs (Eberle et al., 1976).

In very small plants is may be feasible to use granular carbon on a **use** and throw away basis, althugh economics probably favour the use of powdered carbon in a sequential operation. The use of granular activated carbon involves the regeneration and reuse of carbon, with some exceptions. This **regeneration can be carried out with sodium hydroxide** provided that high molecular weight colloids are removed before the treatment of the activated carbon. It is possible with this **chemical regeneration** to *recover phenols*, for example (Jørgensen, 1976), and *to remove coloured bodies* (Chamberlin et al., 1975; Mulligan et al., 1976). Also **solvent** can be used for regeneration of activated carbon, as indicated by Rovel (1972).

When sodium hydroxide or solvent is used, the adsorbate is passed through the carbon bed in the opposite direction to that of the service cycle, until all is removed. The bed is then drained and the regenerated carbon is ready to go back into the stream.

Juhols and Tupper (1969) have studied the **thermal regeneration** of granular activated carbon, which consists of three basic steps, (1) **drying**, (2) **baking of adsorbate** and (3) **activation by oxidation** of the carbon residues from decomposed adsorbates. Drying requires between 100 and 700°C and activation a temperature above 750°C. All three steps can be carried out in a direct fired, multiple hearth furnace. This is the best commercial equipment available for regeneration of carbon for use in combination with waste water treatment. The capacity of the activated carbon will generally decrease by approximately 10% during the first thermal regeneration and another 10% during the next 5-10 regenerations.

6.4.4. Application of chemical Oxidation and Reduction for Treatment of industrial waste water.

By chemical oxidation and reduction the oxidation stage of the substance is changed. Oxidation is a process in which the oxidation stage is increased, while chemical reduction is a process in which the oxidation stage is decreased.

P.6.36. An oxidation-reduction (redox) reaction is defined as a process which electrons are transferred from one substance to another.

An oxidation means loss of electrons and a reduction involves gain of electrons. The concept of electron exchange is very useful because it affords a simple means of balancing redox reactions. With regard to this balancing, the concept of oxidation stage is introduced. The definition of this concept is based on the following rules:

- 1. All elements have an oxidation stage of zero.
- 2. All ions have the same oxidation stage as their charges.

- 3. Hydrogen has the oxidation stage +1 in all its compounds.
- 4. Oxygen has the oxidation stage -2 in all its compounds, except hydrogen peroxide and its derivates.
- 5. The sum of the oxidation stages of all atoms in an uncharged molecule is zero.

To illustrate this point a chlorination can be considered,

e.g. $Cl_2 + C_2H_8 - C_2H_5Cl + HCl.$

In accordance with Pauling (1960), the oxidation number of each atom in a covalent compound is the charge remaining on the atom when each electron pair is assigned completely to the more electro-negative of the atoms sharing the electrons. The three elements involved in the reaction are H, C and CI. The electronegativity of these three elements is, respectively, 2.1, 2.5 and 2.8. This means that C in C_2H_6 has the oxidation stage -3, while in C_2H_5CI it has the oxidation stage -2. In both C_2H_5CI and HCI, CI has the stage -1.

The application of oxidation is largely limited, mainly for the reasons of economics.

Several aspects are considered in the selection of a suitable oxidizing agent for industrial waste water treatment. They are:

- 1. Ideally, no residue of oxygen should remain after the treatment and there should be no residual toxic or other effects.
- 2. The effectiveness of the treatment must be high.
- 3. the cost must be as low as possible.
- 4. The handling should be easy.
- P.6.37. Only a few oxidants are capable of meeting these requirements. The following oxidants are in use today for treatment of water and waste water:
 - 1. Oxygen or air.
 - 2. Ozone.
 - 3. Potassium permanganate.
 - 4. Hydrogen peroxide.
 - 5. Chlorine.
 - 6. Chlorine dioxide.

Oxygen has its significance in **biological oxidation**, but also plays an important role in **chemical oxidation**.

The primary attraction of oxygen is that it can be applied in the form of air. Organic material, including phenol, can be catalytically oxidized by the use of suitable catalysts, such as oxides of copper, nickel, cobalt, zinc, chromium, iron, magnesium, platinum and palladium, but, as yet, this process has not been developed for use on a technical scale.

Ozone is a more powerful oxidant than oxygen and is able to react rapidly with a wide spectrum of organic compounds and microorganisms present in waste water.

It is produced from oxygen by means of electrical energy, which is a highly attractive process since air is used. One of the advantages of using ozone is that it does not impart taste and odour to the treated water. Ozone is used in the following areas of water treatment:

1. Removal of colour, taste and odour (Holluta, 1963).

- 2. Disinfection.
- 3. For the oxidation of organic substances, e.g. phenol, surfactants (Eisenhauer, 1968; Wynn et al., 1972) and cyanides (Anon, 1958; Khandelwal et al., 1959).

The solubility of ozone is dependent upon the temperature. Henry's coefficient as a function of the temperature for ozone and oxygen is shown in Table 6.30.

Henry's coefficient, H, is used in Henry's law (see section 2.5, principle 2.14):

(6.55)

p = H * x

where

p = the partial pressure in atmospheres

x = the mole fraction in solution

Ozone has low thermodynamic stability at normal temperature and pressure (Kirk-Othmer, 1967). It decomposes both in the gas phase and in solution. Decomposition is more likely in aqueous solutions, where it is strongly catalyzed by hydroxide ions, see Table 6.31 (Stumm, 1958).

The oxidation of phenol by gaseous ozone has been studied by Gould et al. (1976) under a number of conditions.

TABLE 6.30

Henry's coefficient for oxygen and ozone in water

	н•	10-4
Temperature (°C)	Oxygen	Ozone
0 5 10 15 20 25 30 35 40 45 50	2.5 2.9 3.3 3.6 4.0 4.4 4.8 5.1 5.4 5.6 5.9	0.25 0.29 0.33 0.38 0.45 0.52 0.60 0.73 0.89 1.0 1.2

TABLE 6.31Influence of pH on half-life ofozone in water (Stumm, 1958)

рН	Half-life (min)
7.6	41
8.5	11
8.9	7
9.2	4
9.7	2
10.4	0.5

Virtually complete removal of phenol and its aromatic degradation products is realized when 4-6 moles of ozone have been consumed for each mole of phenol originally present. At this point approximately 1/3 of the initial organic carbon will remain and 70-80% reduction of the COD-number will have been achieved. Concentrations of the non-aromatic degradation products will be less than 0.5 mg/l. Subsequent dilution of the discharge of this effluent should reduce the concentration of the various components in the receiving body of water to tolerable levels.

Ozone is extremely toxic, having a maximum tolerable concentration of continuous exposure of 0.1 ppm. However, the half-life of ozone is reduced by high pH as demonstrated in Table 6.31.

The ozone concentration can be analyzed either by ultraviolet absorption spectroscopy or by iodide titration:

$$O_3 + 3I^2 + H_2O - I_3^2 + O_2 + 2OH^2$$
 (6.56)

The liberated iodine is titrated with thiosulphate (Kirk-Othmer, 1967). As indicated above, ozone is generated from dry air by a high voltage electric discharge. A potential of 5000 to 40,000 volts between the electrodes is used. Cooling is usually employed to minimize ozone decomposition in the reactor. Theoretically 1058 g of ozone can be produced per kWh of electrical energy, but in practice a production of 150 g/kWh is more usual.

Permanganate is a powerful oxidizing agent and is widely used by many municipal water plants for taste and odour control and for the removal of iron and manganese. Furthermore, it can be used as an oxidant for the removal of impurities such as Fe^{2+} , Mn^{2+} , S^{2-} , CN^{-} and phenols present in industrial waste water.

In strongly acidic solutions permanganate is able to take up five electrons:

$$MnO_4^- + 8H^+ + 5e^- - 4H_2O + Mn^{2+}$$
 (6.57)

While in the pH range from approximately 3 to 12 only three electrons

are transferred and the insoluble manganese dioxide is formed:

$$MnO_4^- + 4H^+ + 3e^- - 2H_2O + MnO_2$$
 (6.58)
or

 $MnO_4^- + 2H_2O + 3e^- - 4OH^- + MnO_2$ (6.59)

The stoichiometry for the oxidation of cyanide in a hydroxide solution of pH 12-14 is:

$$2MnO_4^- + CN^- + 2OH^- - 2MnO_4^{2-} + CNO^- + H_2O$$
 (6.60)

In a saturated solution of calcium hydroxide (Posselt, 1966) the reaction takes the form:

 $2MnO_4^{-} + 3CN^{-} + H_2O - 3CNO^{-} + 2MnO_2 + 2OH^{-}$ (6.61)

The presence of calcium ions affects the rate of manganate(IV) production disproportionately:

$$3MnO_4^{2} + 2H_2O - 2MnO_4^{-} + 4OH^{-} + MnO_2$$
 (6.62)

The permanganate concentration can be determined by spectrophotometry (absorption maximum at 526 μ m or by a titrimetric method.

Table 6.32 gives a survey of the oxidation of organic compounds by permanganate.

Chlorine is known to be a successful **disinfectant** in waste water treatment, but it is also able to oxidize effectively such compounds as **hydrogen sulphide, nitrite, divalent manganese and iron and cyanide**. The oxidation effectiveness usually increases with increasing pH.

Cyanide, which is present in a number of different industrial waste waters, is typically oxidized with chlorine at a high pH.

The oxidation to the much less toxic cyanate (CNO⁻) is generally satisfactory, but in other cases complete degradation of cyanide to carbon dioxide and nitrogen is required.

The disadvantage of chlorine is that it forms aromatic chlorocompounds, which are highly toxic, e.g. chlorophenols, when phenol-bearing water is treated with chlorine (Aston, 1947).

This fact has resulted in the more widespread use of chlorine dioxide. Chlorine dioxide is as unstable as ozone and must therefore be generated in situ.

TABLE 6.32 Permanganate	oxidation of	organic compounds	
		ОН ОН	-
-СН - СН-		-сн - сн-	
R - CH ₂ OH		R - COOH	
R - CHO		R - COOH	
R ₂ - CHOH	·	$R_2 - G = O$	
R - SH		R - SO₃H	
Alkyl amines		R - COOH + NH ₃	
R ₁ - S - R ₂		R ₁ - SO ₃ - R ₂	
R ₁ - S - S - R ₂		R ₁ - SO ₃ H + R ₂ - SO ₃ H	
R1 - SO - R2		R ₁ - SO ₂ - R ₂	

The industrial generation of chlorine dioxide is carried out by means of a reaction between chlorine and sodium chlorite in acid solution (Granstrom and Lee, 1958):

$$CI_2 + 2NaCIO_2 - 2CIO_2 + 2NaCI$$
(6.63)

As chlorine dioxide is a mixed anhydride of chlorous and chloric acid, disproportionation to the corresponding anions occurs in basic solutions:

$$2CIO_2 + 2OH^2 - CIO_2 + CIO_3 + H_2O$$
 (6.64)

This process becomes negligible under acidic conditions. The equilibrium:

$$2CIO_2 + H_2O - HCIO_2 + HCIO_3$$
 (6.65)

shifts to the left at lower pH.

According to Myhrstad and Samdal (1969) chlorine dioxide can be analysed with acid chrome violet K, and determined spectrophotometrically without interference by Cl_2 , ClO^- , ClO_2^- and ClO_3^- .

As iodometric titration gives Cl₂:

$$Cl_2 + 2l^2 - 2Cl^2 + l_2 \quad (pH = 7.0)$$
 (6.66)

and iodometric titration at pH = 2.5-3.0 gives the total amount of $Cl_2 + ClO_2 + ClO_2$

$$CI_{2} + 2I^{-} - 2CI^{-} + I_{2}$$
 (6.67)

 $2CIO_2 + 8H^+ + 10I^- - 2CI^- + 4H_2O + 5I_2$ (6.68)

$$ClO_{2}^{-} + 4H^{+} + 4I^{-} - Cl^{-} + 2H_{2}O + 2I_{2}$$
 (6.69)

it is possible to make a simultaneous determination of CIO_2 , CIO_2^- and CI_2 independently.

Chlorine dioxide is used for taste and odour control. It has been reported to be a selective oxidant for industrial waste water containing cyanide, phenol, sulphides and mercaptans (Wheeler, 1976).

Hydrogen peroxide can be used as an oxidant for **sulphide** in water (Cole et al., 1976). Recently this oxidizing ability has been applied to control odour and corrosion in domestic and industrial waste water.

6.5. REMOVAL OF (HEAVY) METALS.

6.5.1. The problem of heavy metals.

Heavy metals are the most harmful metals, but in the title the word heavy is shown in brackets to indicate that toxic metals other than heavy metals are dealt with in this chapter.

1. Toxic metals are harmful to aquatic ecosystems. (For further details see section 2.1 and 5.4). Treatment by a mechanico-biological process is, to a certain extent, able to remove metals, but the efficiency is only in the order of 30-70%, depending on the metal. The heavy metals removed are concentrated in the sludge, which, even for plants treating solely municipal waste water, shows measurable concentrations (see section 5.4).

As mentioned in 6.3.2, chemical precipitation offers a high efficiency in the removal of heavy metals.

2. Heavy metals are harmful to biological treatment and are example of non-competitive inhibitors. (For further details see 6.4.1).

It is possible, however, according to Neufeld et al. (1975), to grow cultures of activated biota in the presence of mercury, cadmium and zinc levels that are higher than those that would previously have been thought possible. Mercury, cadmium and zinc are rapidly removed from aqueous solutions by biological flocculation. Although the eventual equilibrium was only achieved after about 2-3 weeks, three hours of contact were sufficient almost to reach that equilibrium. The ratio of the weight of metal in the surrounding aqueous phase for the metals mercury, cadmium and zinc at equilibrium, ranges from 4000 to 10,000.

In the main industrial waste water contains harmful concentrations of heavy metals, and consequently these **must be removed** before such waste water is discharged into the municipal sewage system. Only in this way can the two problems mentioned above be solved simultaneously.

P.6.38. Minor amounts of the least toxic metals may be discharged provided their contribution to the concentration in the municipal waste water is of little importance, but as demonstrated in 6.4.1 only a small concentration of toxic metals can be tolerated.

Chiefly, four processes are applied for removal of heavy metals from industrial waste water:

- 1. Chemical precipitation
- 2. Ion exchange
- 3. Extraction
- 4. Reverse osmosis

Adsorption has also been suggested for the removal of mercury by Logsdon et al. (1973). 1 mg per litre of powdered carbon is needed for each 0.1 μ g per litre of mercury to be removed.

It is often economically as well as feasibly, preferable from the resource and ecological point of view, to recover heavy metals. The increasing cost of metals, foreseen in the coming decades, will probably provoke more industries to select such solutions to their waste water problems. *Partial or complete recirculation of the waste water* should also be considered, since a decrease in water consumption and in loss of material is achieved simultaneously; in many cases there is even a considerable saving in water obtained by reorganization of processes.

6.5.2. The application of chemical precipitation for removal of heavy metals.

One of the processes most used for the removal of metal ions from water is precipitation, as metal hydroxide.

Table 6.33 lists the solubility products for a number of metal hydroxides.

Hydroxide	z = charge of metal ions	pK _s
AgOH(1/2 Ag ₂ O) Cu(OH) ₂ Zn(OH) ₂ Ni(OH) ₂ Co(OH) ₂ Fe(OH) ₂ Mn(OH) ₂ Cd(OH) ₂ Mg(OH) ₂ Ca(OH) ₂	1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	7.7 20 17 15 15 15 15 13 14 11
$Al(OH)_3$ Cr(OH)_3	33	32 32 32

TABLE 6.33 pK_s values at room temperature for metal hydroxides pK_s = -log K_s, where K_s = $[Me^{z+}]$ [OH⁻]^z

P.6.39. From the solubility product it is possible to find the pH value at which precipitation will start for a given concentration of the metal ions.

Fig. 6.53 shows the solubilities of metal ions at various pH values. By means of this diagram it is possible to find the concentration in solution at any given pH. For example, at pH 6.0 the concentration of Cr^{3+} is 10^{-6} M. The same concentration for Zn^{2+} is obtained at pH 8.0.

The slopes of the lines in Fig. 6.53 correspond to the valency of the metal ions. The slope of the Cr^{3+} and Al^{3+} lines, for example, is +3, while the other ions in the figure have lines with a slope of +2. This is obtained from the solubility product:

 $[Me^{n+}] [OH^{-}]^{n} = K_{s}$

 $\log [Me^{n+}] = -pK_s + n^*pOH = -pK_s + 14 - n^*pH$ (p = "-log")





From the basis of the solubility product it is possible to find one point though which the line pass. For example, for the solubility product of iron(II) hydroxide, which is 10^{-15} , we have

 $[Fe^{2+}] [OH^{-}]^{2} = 10^{-15}$

The line will therefore go through the point -log c = 5 and pOH = 5 (c = concentration of Fe²⁺), since $(10^{-5})^3 = 10^{-15}$.

Table 6.34 gives the pH value at which the solubility is 10 mg or less of the metal ion per litre and 1 mg or less per litre, respectively.

TABLE 6.34

	So	lubility	
Metal ion	≤ 10 mg/l	_ ≤ 1 mg/l	
Mg ²⁺	11.5	12.0	
Fe ²⁺	8.9	9.4	
Ni ²⁺ Co ²⁺	7.8 7.8	8.3 8.3	
Zn ²⁺ Cr ³⁺	7.2	7.7	
Al ³ + Fe ³⁺	5.0	5.3	

The pH value indicates where the solubility is \leq 10 mg/l and \leq 1 mg/l

From these considerations it is presumed that other ions present do not influence the precipitation, but in many cases it is necessary to consider the ionic strength:

$$I = \sum 1/2 C Z^2$$
 (6.70)

where C = the molar concentration of the considered ions and Z = the charge.

On the basis of the ionic strength, it is possible to find the activity coefficient, f, from

$$-\log f = \frac{0.5 \cdot Z^2 \cdot \sqrt{1}}{\sqrt{1+1}}$$
(6.71)

where

I = ionic strength, Z = charge and f = activity coefficient

TABLE	6.35					
Activity	coefficient	f	at	different	ionic	strengths

	$\frac{\sqrt{1}}{1+\sqrt{1}}$	f for Z = 1	f for Z = 2	f for Z = 3
0 0.001 0.002 0.005 0.01 0.02 0.05 0.1 0.2 0.5	0 0.03 0.04 0.07 0.09 0.12 0.18 0.24 0.31 0.41	1.00 0.97 0.95 0.93 0.90 0.87 0.81 0.76 0.70 0.62	1.00 0.87 0.82 0.74 0.66 0.57 0.43 0.33	1.00 0.73 0.64 0.51 0.40 0.28 0.15 0.10

I = ionic strength, Z = charge, f = activity coefficient

Table 6.35 gives the activity coefficients for different charges of the considered ions, calculated from the equation (6.71).

Since calcium hydroxide is the cheapest source of hydroxide ions, it is most often used for the precipitation of metals as hydroxides. In most cases it is necessary to determine the amount of calcium hydroxide required in the laboratory.

Flocculation is carried out after the addition of the chemical and before settling has occured. If the amount of waste water that must be treated per 24 hr is 100 m³ or less, it is preferable to use a discontinuous treatment. The system in this case consists of two tanks with a stirrer. The waste water is discharged into one tank while the other is used for the treatment process. If chromate is present the treatment processes will follow the scheme below:

- 1. The concentration of chromate and the amount of acid required to bring the pH down to 2.0 are determined.
- 2. On the basis of this determination the required amounts of acid and reducing compound are added (about the reduction, see below).
- 3. Stirring 10-30 minutes.
- 4. The concentration of chromate remaining is determined and the pH checked. If chromate is present further acid or reducing agent is added. In this case the stirring (10-30 minutes) must be repeated.
- The amount of calcium hydroxide necessary to obtain the right pH for precipiation is measured. If Cr³⁺ is present a pH value of 8-9.5 is normally required.
- 6. Flocculation 10-30 minutes.
- 7. Settling 3-8 hours.
- 8. The clear phase is discharged into the sewer system. The sludge can be concentrated further by filtration or centrifugation.

Stages 1-5 can, of course, be left out if chromate is not present, and the metal ions can be directly precipitated.

P.6.40. Reduction is a process in which soluble metallic ions are reduced through a redox reaction.

Generally, the process is used in the treatment of plating waste water containing chromate. This water, from chromate acid baths used in electroplating and anodizing processes, contains chromate in the form of CrO_3 or $Na_2Cr_2O_7$, $2H_2O$. The pH of such waste water is low and the Cr(IV) concentration is often very high - up to 20,000 ppm or more. The most commonly used reducing agents are iron(II) sulphate, sodium meta-hydrogen sulphite or sulphur dioxide. Since the reduction of chromate is most effective at low pH, it is, of course, an advantage if the waste water itself contains acid, which is often the case. Iron(II) ions react with chromate by reducing the chromium to a trivalent state and the iron(II) ions are oxidized to iron(III) ions.

The reaction occurs rapidly at a pH below 3.0, but since the acidic properties of iron(II) sulphate are low at high dilution, acid must often be added for pH adjustment. The reactions are:

It is possible to show that 1 mg of Cr will require 16 mg $FeSO_4$, $7H_2O$ and 6 mg of H_2SO_4 , based on stoichiometry.

Reduction of chromium can also be accomplished by the use of meta-hydrogen sulphite or sulphur dioxide. When meta-hydrogen sulphite is used, the salt hydrolyzes to hydrogen sulphite:

$$S_2O_5^{2^*} + H_2O - 2HSO_3^{-1}$$
 (6.75)

The hydrogen sulphite reacts to form sulphurous acid:

$$HSO_3^- + H_2O - H_2SO_3 + OH^-$$
 (6.76)

Sulphurous acid is also formed when sulphur dioxide is used, since:

$$SO_2 + H_2O - H_2SO_3$$
 (6.77)

The reaction is strongly dependent upon pH and temperature. The redox process is:

$$2H_2CrO_4 + 3H_2SO_3 - Cr_2(SO_4)_3 + 5H_2O$$
 (6.78)

Based on stoichiometry, the following amounts of chemicals are required for 1 mg of chromium to be precipitated: 2.8 mg $Na_2S_2O_5$ or 1.85 mg SO_2 .

Since dissolved oxygen reacts with sulphur dioxide, excess SO_2 must be added to account for this oxidation:

$$H_2SO_3 + 1/2O_2 - H_2SO_4$$
 (6.79)

If the amount of waste water exceeds 100 m^3 in 24 hr, the plant shown in Fig. 6.54 can be used.

A potentiometer and pH meter are used to control the addition of acid and reducing agent. These instruments can be coupled to an automatic dosing control. As seen from the figure, the plant consists of a reaction tank, a flocculation tank and a sedimentation tank. Usually a settling time of 24 hr or more is used.

A concentration of 1 1/3 - 3% dry matter for the sludge is usually obtained, which is slightly less than that obtained by discontinuous treatment.



Fig. 6.54. Flowchart of a plant for precipitation of metal ions. This plant includes the reduction of chromate to Cr^{3+} .

Fig. 6.55 shows the so-called Lancy system for treating waste water containing chromate.

This system contains a recirculation tank connected to the reduction tank as well as to the precipitation tank. Filtration of the sludge is continuous and 20-35% dry matter is obtained.

Thomas and Theis (1976) have shown that the coagulation and settling of colloidal chromium(III) hydroxide are functions of both the quantity and type of impurity ions present.

The treatment might not operate effectively because of the complexing or stabilizing effects of high carbonate or pyrophosphate concentrations in the water.

It is possible to eliminate the problem caused by carbonate and phosphate by modifying the treatment scheme for the combined waste. Prime consideration should be given to the modification consisting simply of using lime instead of caustic soda to neutralize the waste after the chemical reduction of chromate to chromium(III) has taken place. The use of lime will cause precipitation and removal of most of the carbonate and pyrophosphate species from the solution while also providing doubly charged counter-ions to aid in coagulating the negatively charged chromium(III) hydroxide colloids that exist at pH values of about 8.

Other treatment modifications, such as the use of polyelectrolytes to flocculate the stabilized chromium(III) hydroxide system, may or may not be effective alternatives, depending on the amount of complexation present in a particular waste system.



Fig. 6.55. The Lancy system.

Data presented indicate that a hydrogen carbonate alkalinity of 250 mg/l as $CaCO_3$ and a pyrophosphate concentration of 30 mg/l as P together cause appreciable complexation and may make alternatives other than lime neutralization impractical.

The formation of calcium carbonate flocs during lime neutralization could also aid in the removal of chromium(III) hydroxide colloids by the enmeshment mechanism and, at the same time, make the resulting sludge easier to dewater because of the presence of the large volume of calcium carbonate. The increased treatment efficiency and better sludge handling characteristic may make the use of lime a more favourable solution even though the quantity of sludge may be somewhat increased.

The last treatment modification to be considered is the use of Fe^{2+} ions as the reducing agent in the chromate-reduction step. The end product of this reaction is Fe^{3+} ions. In the neutral pH range this is very effective in removing chromium(III) hydroxide colloids.

6.5.3. The application of Ion Exchange for Removal of Heavy Metals.

P.6.41. A cation exchanger can be used for the removal of metal ions from waste water, such as Fe²⁺, Fe³⁺, Cr³⁺, Al³⁺, Zn²⁺, Cu²⁺, etc. (Spanier, 1969)

The most common type of cation exchanger consists of a polystyrene matrix, which is a strong acidic ion exchanger containing sulphonic acid groups:



The practical capacity of the cation exchanger is 1-1.5 eqv/l of ion exchang material (Rüb, 1969). To ensure high efficiency, a relatively low flow rate is recommended, often below 5 bed volumes/hour.

A recent development has brought a starch xanthate and a cellulose polyethyleneimine ion exchanger onto the market (WRL, 1977). They have a lower capacity than the conventional cation exchangers, but since they are specific for heavy metal ions they have a higher capacity when measured as the volume of water treated between two regenerations per volume of ion exchanger.

It is often preferable to separate waste water from the chromate baths and the rinsing water, since this opens up the possibility of reusing the water. *Chromate can be recovered* and the waste water problem can be solved in an effective way (Mohr, 1969).

Fig. 6.56 is a flow diagram of an ion exchange system in accordance with these principles.

Reuse of the elution liquid from the anion exchanger and of the treated waste water might be considered.

The pH of the elution liquid from the cation exchanger must be adjusted and the metal ions precipitated for removal by the addition of calcium hydroxide (see Fig. 6.56).



chromic acid

Fig. 6.56. Ion exchange of waste water containing chromate. (1) Cation exchanger; (2) Precipitation tank; (3) Anion exchanger; (4) Exchange of Na⁺ with H⁺.

In some instances it is too costly to seperate the different types of waste water and rinsing water. In such cases a simpler ion exchange system is used (Schaufler, 1969), although it is, of course, possible to recover the chromate from the elution liquid.

Since, as well as inorganic impurities, the waste water contains organic material, such as oil, fat, dust, etc., the ion exchanger often becomes clogged if the waste water is not pretreated before being passed into the ion exchange system. *Macroporous ion exchangers* have only partly solved this problem since suspended matter, emulsions and high molecular weight organic compounds will also affect this type of ion exchanger.

Consequently, it is an advantage to pretreat the waste water on sand filters or activated carbon. The sand filter will remove the suspended particles and the activated carbon most of the organic impurities.

Since most of the ions are eluted in the first 60-75% of the eluting volume, it is often of advantage to use the last portion for the subsequent regeneration.
6.5.4. The application of extraction for removal of heavy metals.

P.6.42. Most heavy metal ions can be recovered from aqueous solutions by extraction. Complexes of the metal ions are formed, for example by reaction with CI⁻, and these metal complexes are then extracted by means of organic solvents.

By using different concentrations of the ligand it is possible to separate different metals by extraction, again opening up the possibility of recovering the metals. The calculation of the equilibrium is based on the following reactions:

From reaction (6.80) and by using the mass action law it is possible to set up the following expression:

$$\frac{[Me L]}{[L] [Me]} = K$$
(6.82)

Reaction (6.81) can be quantitatively expressed by means of the distribution coefficient, D, where:

$$d = \frac{[Me L]_{organic solvent}}{[Me L]_{water}}$$
(6.83)

Combining equations (6.82) and (6.83) gives:

$$K * D = \frac{[Me]_{org.}}{[L] [Me]}$$
 (6.84)

where [Me]_{org.} is the total metal ion concentration in the organic phase. By applying this reaction in practice it is possible to vary both the concentration of the ligand, and the volume of the organic phase.

On increasing the concentration of the ligand and increasing the volume of the organic phase, [Me]_{org.} will increase and [Me] decrease (see equation (6.83) and (6.84)).



Fig. 6.57. Efficiency of extraction against Cl⁻ concentration.

Fig. 6.57 shows the extraction efficiency of various concentrations of chloride for several metal ions. These calculations are based upon the application of the same volume of organic solvent as the waste water treated. As seen form the diagram, it is possible, for example, to separate Fe^{2+} ions from cobalt by extracting with 60 g Cl⁻/l. The extraction can also be carried out by a liquid ion exchanger of the trialkylamine type R_3NHCI .

The extraction process for FeCl_4 in aqueous solution will take place according to the following reactions:

$$FeCl_{4}(aq) + R_{3}NHCl(org) - R_{3}NHFeCl_{4}(org) + Cl^{-}(aq)$$
 (6.85)

Recovery of copper from a solution containing Cu^{2+} , SO_4^{2-} , Na⁺ and H⁺ (pH = approx. 2.0) is possible by extraction with acetone. The efficiency should be 99.9% according to patent DDR 67541. On recovering the acetone by distillation a loss of 0.3 kg acetone/100 kg copper is recorded.

An amine extraction process has also been developed for the recovery of cyanide and metal cyanide from waste streams of plating processes (Chemical Week, 1976).

6.5.5. Application of membrane process for removal of heavy metals.

Membrane separation, electrodialysis, reverse osmosis, ultrafiltration

and other such processes are playing an increasingly important role in waste water treatment.

A membrane is defined as a phase which acts as a barrier between other phases. It can be a solid, a solvent-swollen gel or even a liquid. The applicability of a membrane for separation depends on differences in its permeability to different compounds.

Table 6.36 gives a survey of membrane separation processes and their principal driving forces, applications and their useful ranges.

Process	Driving force	Range (µm) particle size	Function of membrane	
Electrodialysis	Electrical poten- tial gradient	< 0.1	Selective to certain ions	
Dialysis	Concentration	< 0.1	Selective to solute	
Reverse osmosis	Pressure	< 0.05	Selective transport of water	
Ultrafiltration	Pressure	5 • 10 ⁻³ - 10	Selective to mole- cular size and shape	

TABLE 6.36 Membrane separation processes

Osmosis is defined as a spontaneous transport of a solvent from a dilute solution to a concentrated solution across a semi-permeable membrane. At a certain pressure - the so-called osmotic pressure - equilibrium is reached.

The osmotic pressure can vary with concentration and temperature, and depends on the properties of the solution.

For water, the osmotic pressure is given by:

$$\pi = \frac{n}{V} R T \tag{6.86}$$

where

- n = the number of moles of solute
- V = the volume of water
- R = the gas constant
- T = the absolute temperature

This equation describes an ideal state and is valid only for dilute solutions. For more concentrated solutions the equation must be modified by the van Hoff factor by using an osmotic pressure coefficient:

$$\pi = \emptyset + \frac{n}{\nabla} R T$$
 (6.87)

For most electrolytes the osmotic pressure coefficient is less than unity and will usually decrease with increasing concentrations. This means that equation (6.86) is usually conservative and predicts a higher pressure than is observed.

P.6.43. If the pressure is increased above the osmotic pressure on the solution side of the membrane, as shown in Fig. 6.58, the flow is reversed. The solvent will then pass from the solution into the solvent. This is the basic concept of reverse osmosis.

Reverse osmosis can be compared with filtration, as it also involves the moving of liquid from a mixture by passing it through a filter.



Fig. 6.58. A - illustrates equilibrium. An osmotic pressure appears. B - illustrates the principle of reverse osmosis.

However, one important difference is that the osmotic pressure, which is very small in ordinary filtration, plays an important role in reverse osmosis. Second, a filter cake with low moisture content cannot be obtained in reverse osmosis, because the osmotic pressure of the solution increases with the removal of solvents. Third, the filter separates a mixture on the basis of size, whereas reverse osmosis membranes work on the basis of other factors. Reverse osmosis has sometimes also been termed hyperfiltration.

The permeate flux, F, through a semipermeable membrane of thickness, d, is given by:

$$F = \frac{D_W + C_W + V}{R T d} (\Delta P - \pi)$$
(6.88)

where $D_W =$ the diffusion coefficient $D_W =$ the concentration of water V = the molar volume of water $\Delta P =$ the driving pressure (see Fig. 6.58)

The equation (6.88) indicates that the water flux is inversely proportional to the thickness of the membrane. These terms can be combined with the coefficient of water permeation, W_{p} , and equation (6.88) reduces to:

$$F = W_{p} \bullet (\Delta P - \pi)$$
 (6.89)

where

$$W_{p} = \frac{D_{W} + C_{W} + V}{RTd}$$
(6.90)

For the solute flux, F_s , the driving force is almost entirely due to the concentration gradient across the membrane, which leads to the following equation (Clark, 1962):

$$F_{s} = D_{s} \frac{dC'_{i}}{dx} = D_{s} \frac{\Delta C'_{i}}{d}$$
(6.91)

where

 C'_i = the concentration of species, i, within the membrane $\Delta C'_i$ = measured across the membrane

In constructing a system for reverse osmosis many problems have to be solved:

- 1. The system must be designed to give a high liquid flux reducing the concentration potential.
- 2. The packaging density must be high to reduce pressure vessel cost.
- 3. Membrane replacement costs must be minimized.
- 4. The usually fragile membranes must be supported as they have to sustain a pressure of 20-100 atmospheres.

Four different system designs have been developed to meet the solution to the latter problem. The plate and frame technique, large tube technique, spiral wound technique and the hollow fine fibre technique.

The various techniques are compared in Table 6.37.

Module concept	Packing density (m ² /m ³)	Useful pH range	Ease of cleaning	NaCl rejection	Water flux at 40 atm. (m ³ /m ² /day)
Plate and frame	450	2 - 8	fair	very good	0.5
Large tubes	150	2 - 8	very good	very good	0.5
Spiral	750	2 - 8	good	very good	0.5
Hollow fine fibres	7500 - 15000	0 - 12 ^{*)}	fair	good/fair	0.05 - 0.2

TABLE6.37Comparison of the various techniques

*) Polyamide

The most widely used membrane is the *cellulose acetate membrane* in the Loeb-Sourirajan technique. This membrane is asymmetrical and consists of a thin dense skin of approximately 0.2 μ m on an approximately 100 μ m thick porous support.

As shown in Fig. 6.59, these membranes are not resistant to high or low pH, and a temperature range of 0-30°C must be recommended.



Fig. 6.59. Hydrolysis rate of cellulose acetate membrane as function of pH at 20°C and 80°C. (Vos et al., 1966).

Polyamide membranes have also been developed. They are considerably more resistant to temperature and pH, but give a smaller flux. During the laste decade there has been intense research activity in the development of membranes, resulting in several new types. Cellulose acetate-butyrate resin, cellulose acetat-methacrylate, polyacrylacid and cellulose nitrate-acetate, are among the recently developed membrane materials, which are more resistant to pH and temperature, but do not reduce the initial fluxes. Several natural materials could also be of use as membranes and extensive laboratory investigations may hold promise for the application of such natural membranes in the near future (Kraus et al., 1967).

Reverse osmosis is particularly well suited for the treatment of *nickel-plating rinsing water*.

Cellulose acetate membranes are recommended (Hauck et al., 1972). The treatment can contribute significantly to both *water pollution control and recovery of nickel.*

Push et al. (1975) have demonstrated that it is possible to fractionate metal salts by reverse osmosis.

By tailoring membranes for specific applications and by optimizing the process parameters, such as pressure applied, solute concentrations, and added polyelectrolyte, it is possible to fractionate metals from waste water and recover valuable materials.

By using polyamide membranes for reverse osmosis experiments at 100 atmospheres with an equimolar solution of $AgNO_3$ and $Al(NO_3)_3$, the membrane was able to reject 99.98% of aluminium salt, while the silver salt was enriched in the permeate.

6.6. WATER RESOURCES.

6.6.1. Introduction.

P.6.44. Man cannot exist without water, so there has always been a demand for water and all the nearest and more obvious sources have already been exploited. Any future demand must inevitably be met from more remote and increasingly less attractive sites, and for this reason alone development costs must rise continuously in the future.

The relationship between the hydraulic cycle and the water demand now and in the near future has already been touched on in section 2.11. Most waters have to be purified before they can be used for human consumption. Raw water is so infinitely variable in quality that there is no fixed starting point in the treatment process. Many countries have their own standards of acceptable purity for potable water and these vary. WHO lays down two standards (see Appendix 6), which are widely applied in developing countries.

P.6.45. Virtually no water is impossible to purify to potable standards, but some raw waters are so bad as to merit rejection, because of the expense involved. Water from underground sources is generally of better quality than surface water, but it may be excessively hard and/or contain iron and manganese. Full treatment of water may comprise pretreatment, mixing, coagulation, flocculation, settling, filtration and sterilization. Not all waters require full treatment, however.

The difference of the two sources are summarized in Table 6.38.

Pretreatment includes screening, raw water storage, prechlorination, aeration, algal control and straining.

As coagulants aluminium sulphate, sodium aluminate and iron salts are used. They are usually applied in combination with coagulant acids, which include lime, sodium carbonate, activated silica and polyelectrolytes. After coagulation, mixing, flocculation, and sedimentation, take place, as described in 6.2.2 and 6.3.2 respectively.

For filtration sand filters are widely used either after coagulation, mixing, flocculation and sedimentation of surface water or after aeration of ground water for removal of iron and manganese compounds.

TABLE 6.38		_		_			
Characteristics	of	ground	water	and	surface	water	

Properties	Ground water	Surface water	
Salt concentration Iron concentration Manganese concentration KMnO ₄ number Hardness pH Turbidity Temperature Number of E. coli Colour	high high low high 6-8 low low low 0 none	low low high low 7-9 high high >0 yellowish	

Two typical flow diagrams for treatment of ground and surface water are shown in Figs. 6.60 and 6.61. Most of the processes used in water treatment have already been mentioned (see Table 6.2).

However, softening and disinfection are treated in the following paragraphs.







- Fig. 6.61. Typical treatment of ground water.
- P.6.46. Water management is closely linked to waste water management (see section 6.1). Insufficient treatment of waste water can have several consequences, of which two will be mentioned:
 - low quality surface water that requires a more advanced treatment of the raw water for production of potable water,
 - the treated waste water is discharged to the sea to avoid a deterioration of the quality of the surface water. Consequently, it is necessary to use supplementary sources of raw water, which may be difficult close to cities, or areas suffering from water shortage.

6.6.2. Softening.

The presence of polyvalent cations in water causes hard water, so called because it is hard to form a lather with soap. Polyvalent salts of the long-chain fatty acids present in soap are insolubel. In the days when all washing was done with soaps, the problem of hard water was more of a niusance than it is today, when soaps have been replaced largely with synthetic detergents, whose polyvalent metal salts are relatively soluble. The predominant metal ions in waters used for potable supplies are calcium and magnesium.

- P.6.47. Hardness can be either calcium hardness (including magnesium hardness), temporary hardness, which is carbonate and hydrogen carbonate hardness, or permanente hardness, which is the difference between the calcium hardness and the temporary hardness, i.e. calcium hardness that has no carbonate or hydrogen carbonate as counter ions.
- P.6.48. Temporary hardness can be removed by boiling the water, since:

$$Ca(HCO_3)_2 - CaCO_3 + CO_2 + H_2O$$
 (6.92)

Hardness is often quantified as calcium carbonate equivalents in mg per litre or as hardness degrees, which uses 10 mg I^{-1} CaO as its base unit. The content of magnesium ions is taken into consideration by calculating th equivalent amount of calcium carbonate and calcium oxide, respectively. It turns out that 83 mg of magnesium carbonate correspont to 100 mg calcium carbonate and 39 mg of magnesium oxide give the same number of hardness degrees as 56 mg of calcium oxide = 5.6 degrees of hardness.

P.6.49. There are two principal methods of softening water for municipal purposes; by lime and lime-soda and ion exchange.

The first method is based upon precipitation of calcium as calcium carbonate and magnesium as magnesium hydroxide.

A classification of water in terms of hardness is given in Table 6.39.

The lower limits of softening by this process are based on the solubilities of these precipitates, see Table 6.40.

When lime is used, only the carbonate hardness is reduced. The additional use of soda can reduce the permanent hardness as well.

TABLE 6.39Classification of water in terms of hardness

mg/l calcium carbonate	Hardness degrees	Specification
0 - 80	0 - 4	Very soft
80 - 160	4 - 8	Soft
160 - 240	8 - 12	Medium hard
240 - 600	12 - 30	Hard
>600	>30	Very hard

TABLE 6.40

Solubilities of $CaCO_3$ and $Mg(OH)_2$ as functions of temperature and pH

рН	CaCO ₃ solubility mg/l		Mg(OH) ₂ solut	pility mg/l
	25°C 60°C		25°C	60°C
7 8 9 10 11 12	970 79 8.0 1.0 0.4 0.3	240 20 2.1 0.3 0.13 0.11	- 13,000 130 1.3 0.01	- 5500 55 0.6 very low

The process can be described in five steps:

1. The reaction between free carbon dioxide and added lime:

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$$
 (6.93)

2. The reaction of calcium carbonate hardness with lime:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$
(6.94)

3. The reaction of magnesium carbonate hardness with lime:

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow CaCO_3 + MgCO_3 + 2H_2O$$
(6.95)

$$MgCO_3 + Ca(OH)_2 \rightarrow CaCO_3 + Mg(OH)_2$$
 (6.96)

Combining the above two equations gives:

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + Mg(OH)_2 + 2H_2O$$
 (6.97)

From these equations it can be concluded that 2 moles of lime are required to remove 1 g atom of magnesium, or twice as much as is required for calcium removal.

4. Non-carbonate calcium hardness is removed by soda. The reaction is:

$$CaSO_4 + Na_2CO_3 - CaCO_3 + Na_2SO_4$$
(6.98)

The non-carbonate hardness is represented here as sulphate.

5. The reaction of non-carbonate magnesium hardness with lime and soda is:

$$MgSO_4 + Ca(OH)_2 + Mg(OH)_2 + CaSO_4$$
(6.99)

$$CaSO_4 + Na_2CO_3 + CaCO_3 + Na_2SO_4$$
(6.100)

From these reactions it can be seen that the addition of lime always serves three purposes and may serve a fourth. It removes, in order, carbon dioxide, calcium carbonate hardness and magnesium carbonate hardness. Furthermore, when magnesium non-carbonate hardness must be reduced, lime converts the magnesium hardness to calcium hardness. Soda then removes the non-carbonate hardness in accordance with equations (6.98) and (6.99).

Since softening is usually accomplished at high pH values and the reactions do not go to completion, the effluent from the treating unit is usually supersaturated with calcium carbonate. This would cement the filter medium and coat the distribution system. In order to avoid these problems, the pH must be reduced, so that insoluble calcium carbonate can be converted to the soluble hydrogen carbonate. This is accomplished in practice by recarbonation, i.e. the addition of carbon dioxide. The equations may be as follows:

$$CaCO_3 + CO_2 + H_2O + Ca(HCO_3)_2$$
 (6.101)
 $CO_3^{2-} + CO_2 + H_2O + 2HCO_3^{-}$ (6.102)

The large amount of sludge containing calcium carbonate and magnesium hydroxide, produced by softening plants, presents a disposal problem, since it can no longer be discharged into the nearest stream or sewer. Some of this sludge can be recycled to improve the completeness of reaction, but a large quantity must be disposed of. The methods used are lagooning, drying for land fill, agricultural liming and lime recovery by recalcination.

In ion exchange softening, the calcium and magnesium ions are exchanged for monovalent ions, usually sodium and hydrogen. This is termed "cation exchange softening", and current practice uses ion exchange resins based on highly cross-linked synthetic polymers with a high capacity for exchangeable cations. In cases where a complete demineralization is required anion exchangers are also employed. In this case, chloride, hydrogen carbonate and other anions are replaced by hydroxide ions, which together with the hydrogen ions released by the cation exchanger, form water:

$$OH^- + H^+ - H_2O$$
 (6.103)

A comparison of the various softening processes is illustrated in Table 6.41.

Comparison of	various softening	processes		
	Lime - soda Cold Hot	lon exchange Na ⁺ -form	H+-forr	n
Min. hardness attainable	30 mg/l	10 mg/i	0	0
Total dissolved solids	Decreased	Decreased	Increased slightly	Decreased
Na-content	?	?	Increased	Decreased significantly
Operation cost	low	low	slightly	higher
Capital	high	high	low	low

TABLE 6.41 Comparison of various softening process

6.6.3. Disinfection processes.

Micro-organisms are destroyed or removed by a number of physicochemical waste water treatment operations, such as coagulation, sedimentation, filtration and adsorption.

However, inclusion of a disinfection step has become common practice in water and waste water treatment to ensure against transmission of waterborne diseases. The disinfection process must be distinguished from sterili- zation. Sterilization involves complete destruction of all micro-organisms including bacteria, algae, spores and viruses, while disinfection does not provide for the destruction of all micro-organisms, e.g. the hepatitis virus and polio virus are generally not inactivated by most disinfection processes.

P.6.50. The mechanism of disinfection involves at least two steps:

- 1. Penetration of the disinfectant through the cell wall.
- 2. Reaction with enzymes within the cell (Fair et al., 1968)

Chemical agents, such as ozone, chlorine dioxide and chlorine, probably cause disinfection by direct chemical degradation of the cell matter, including the enzymes, while application of thermal methods or degradation accomplish essentially physical destruction of the micro-organisms.

The large number of organic and inorganic chemicals exert a poisoning effect on the micro-organisms by an interaction with enzymatic proteins or by disruptive structural changes within the cells.

P.6.51. The rate of destruction of micro-organisms has been expressed by a first order reaction referred to as Chick's law:

$$\frac{dN}{dt} = -k * N$$
 (6.104)

where N is the number of organisms per volume and k is a rate constant. By intetration between the limit t = 0 and t

$$\int_{N_0}^{N(t)} \frac{1}{N} + \frac{dN}{dt} + dt = -k \int_0^t dt$$
 (6.105)

or

$$\ln \frac{N(t)}{N_0} = -kt$$
 (6.106)

$$N = N_0 * e^{-kt}$$
 (6.107)

Rearrangement of this equation and conversion into common logarithms gives:

$$t = \frac{2.3}{k} + \log \frac{N_0}{N(t)}$$
(6.108)

As seen, Chick's law states that the rate of bacterial destruction is directly proportional to the number of organisms remaining at any time. This relationship indicates a uniform susceptibility of all species at a constant concentration of disinfectant, pH, temperature and ionic strength. Many deviations from Chick's law have been described in the literature. In accordance with Fair et al. (1968) chlorination of pure water shows typical deviations from Chick's law, as seen in Fig. 6.62. Often deviation from the first order rate expression is due to autocatalytic reaction. In this case the expression can be transformed to:

$$-\frac{dN}{dt} = k_1 * N(t) + k_2 * N(t) * (N_0 - N(t))$$
(6.109)



Fig. 6.62. Length of survival of E. coli in pure water at pH 8.5 and 2-5°C.

As pointed out the disinfection rate expression (Chick's law) does not include the effect of disinfectant concentration. The relationship between disinfectant concentration and the time required to kill a given percentage of organisms is commonly given by the following expression:

$$C^n \cdot t = constant$$
 (6.110)

Berg (1964) has shown that the concentration/time relationship for HOCI at 0-6°C, to give a 99% kill of Esch. coli is expressed as:

 $C^{0.86} \cdot t = 0.24 \text{ (mg} |^{-1} \text{ min})$ (6.111)

Temperature influences the disinfection rate first, by its direct effect on the bacterial action and second, by its effect on the reaction rate. Often an empirical temperature expression is used, such as:

$$k_t = k_{20} * d^{(t-20)}$$
 (6.112)

where

 $k_t =$ the rate constant at t°C $k_{20} =$ the rate constant at 20°C d = an empirical constant

P.6.52. Most micro-organisms are effectively killed by extreme pH conditions, i.e. at pH below 3.0 and above 11.0.

The effect of disinfection is also strongly dependent on the coexistence of other matter in the waste water, e.g. organic matter. The disinfectant may (1) react with other species to form compounds which are less effective than the parent compounds, or (2) chemically oxidize other impurities present in the water, reducing the concentration of the disinfectants.

The application of heat is one of the oldest, and at the same time most certain, methods of water disinfection. In addition, *freezing and freezedrying are effective methods for the preservation of bacteria*. However, these techniques are of little practical significance for waste water treatment, as they are too costly. Disinfecting large volumes of water by heating is clearly not suitable for economic reasons.

The wave length region from 250-265 nm, beyond the visual spectrum, has bactericidal effects.

Mercury vapour lamps emit a narrow band at 254 nm and can be used for small-scale disinfection. It is assumed that the nucleic acids in bacterial cells absorb the ultraviolet energy and are consequently destroyed. These nucleic acids include deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). The main problem in the application of ultraviolet irridation for disinfection is to ensure that the energy is delivered to the entire volume of the water. Even distilled water will absorb only 8% of the applied energy to a depth of 3 cm, and turbidity, dyes and other impurities constitute barriers to the penetration of ultraviolet radiation.

This means that only a thin layer of clear water without impurities, able

to absorb the ultraviolet light, can be treated. For a 99% level of kill, the use of a 30 W lamp would allow flows of from 2 to $20 \text{ m}^3/\text{hr}$ to be disinfected. The use of ultraviolet lamps for disinfection has some important advantages. As nothing is added to the water no desirable qualities will be changed. No tastes or odours result from the treatment. The disadvantage of ultraviolet irradiation is that it provides no residual protection against recontamination as the application of chlorine does.

Gamma and X rays are electromagnetic radiations of very short wavelength and have an excellent capacity for destroying microorganisms. However, their use is relatively expensive. The application of the method requires care, and this will restrict its use considerably.

Chlorine is produced exclusively by electrolytic oxidation of sodium chloride in aqueous solutions:

$$2Cl^{-} + Cl_{2} + 2e^{-} \tag{6.113}$$

After generation, the chlorine gas is purified by washing in sulphuric acid and the product usually has a purity of more than 99%. The gas is liquefied by compression to 1.7 atmospheres between -30°C and -5°C, and stored in steel cylinders or tanks. Chlorine should be handled with caution, as the gas is toxic and has a high chemical activity, with danger of fire and explosion. In the presence of water chlorine is highly corrosive.

When chlorine is added to an aqueous solution it hydrolyzes to yield Cl⁻ and OCl⁻:

$$Ci_2 + 2H_2O + H_3O^+ + C\Gamma + HOCI$$
 (6.114)

As can be seen, the process is a disproportionation, since chlorine in zero oxidation state turns into oxidation states -1 and +1.

Hypochlorous acid is a weak acid:

$$HOCI + H_2O - H_3O^+ + OCI^-$$
(6.115)

The acidity constant Ka:

$$K_{a} = \frac{[H_{3}O^{+}] [OC|^{-}]}{[HOC|]}$$
(6.116)

is dependent on the temperature as illustrated in Table 6.42.

HOCI is a stronger disinfectant than OCI⁻ ions, which explains why the disinfection is strongly dependent on pH.

Fig. 6.63 shows the time/concentration relationship in disinfection with

chlorine (after Fair et al., 1968).

TABLE 6.42

Temperature	К _а	
0	1.5 • 10 ⁻⁸	
5	1.7 • 10 ⁻⁸	
10	2.0 * 10 ⁻⁸	
15	2.2 * 10 ⁻⁸	
20	2.5 • 10 ⁻⁸	
25	2.7 • 10 ⁻⁸	

The acidity constant for HOCI

The ammonium present in the water is able to react with the chlorine or hypochlorous acid (see 6.3.5).



Fig. 6.63. Concentration of free available chlorine required for 99% kill of E. coli at 2-5°C.

The rates of chlorine formation depend mainly on pH and the ratio of the reactants employed. Moore (1951) infers that the distribution of chlorine is

based on the equation:

$$2NH_{2}CI + H_{3}O^{+} + NH_{4}^{+} + NHCl_{2} + H_{2}O$$
 (6.117)

for which:

$$K = \frac{[NH_4^+] [NHCl_2]}{[H_3O^+] [NH_2Cl]^2} = 6.7 * 10^5 (25^{\circ}C)$$
(6.118)

The disinfection power of chloramines measured in terms of contact time for a given percentage kill, is less than that of chlorine. This is seen by comparing Fig. 6.63 with Fig. 6.64.



Fig. 6.64. Concentration of combined available chlorine required for 50% kill of E. coli at 2-5°C.

The bacterial properties of chlorine are probably based on the formation of free hypochlorous acid:

$$NH_2CI + H_2O + HOCI + NH_3$$
 (6.119)

 $NH_2CI + H_3O^+ + HOCI + NH_4^-$ (6.120)

However, the reaction of chlorine with ammonia or amino compounds presents a problem in the practice of chlorination of waste water containing such nitrogen compounds.



Fig. 6.65. Breakpoint chlorination.

Fig. 6.65 shows the residual chlorine as a function of the chlorine applied. Between points 1 and 2 in the figure, mono- and di-chloramine are formed. The oxidation processes with chlorine occurring between points 2 and 3 give a decline in residual chlorine. Point 3 is called the breakpoint. Addition of chlorine in this interval probably produces free nitrogen gas as the predominant product of oxidation. Fair et al. (1968) even propose that the reaction involving the formation of NOH as an intermediate, followed by the formation of nitric oxide, NO, could explain the observations between points 2 and 3:

$$2NHCl_{2} + 6H_{2}O + 2NOH + 4H_{2}O^{+} + 4C\Gamma$$
 (6.121)

$$2NOH + HOCI + 2NO + H_{2}O^{+} + CI^{-}$$
(6.122)

In total:

$$2NHCl_{2} + HOCl + 6H_{2}O + 2NO + 5H_{3}O^{+} + 5Cl^{-}$$
 (6.123)

Further addition of chlorine beyond the breakpoint gives an increasing residue of free chlorine.

Chlorine doses below the breakpoint requirement can be used to oxidize ammonia if chlorination is followed by contact with activated carbon (Bauer et al., 1973).

Dichloramine has been shown to be rapidly converted to the end product, the most likely reaction being:

$$C + 2NHCl_{p} + H_{p}O + N_{p} + 4H^{+} + 4Cl^{-} + CO$$
 (6.124)

Further study is, however, needed to show conclusively that surface oxidation results from this reaction. Furthermore, it is important to know that the CI_2/NH_4 -N oxidized mole ratio is 2:1, which is required for ammonium oxidation by this pathway.

The monochloramine reaction with carbon appears more complex. On fresh carbon the reaction is most probably:

$$NH_{2}CI + H_{2}O + C + NH_{3} + H^{+} + C\Gamma + CO$$
 (6.125)

After this reaction has proceeded to a certain extent, partial oxidation of monochloramine is observed. Possibily according to the reaction:

$$2NH_{2}CI + CO + N_{2} + H_{2}O + 2H^{+} + 2CI^{-} + C$$
 (6.126)

It has been observed that acclimation of fresh carbon is necessary before monochloramine can be oxidized.

In the removal of ammonia with a dose of chlorine less than the breakpoint followed by contact with activated carbon, pH control can be used to determine the major chlorine species. The studies reported here indicate that a pH value near 4.5 should be avoided, because $NHCl_2$ predominates and thus 10 parts by weight or chlorine are required for each part of NH_3 -N oxidized to N₂. At a slightly higher pH and acclimated carbon, the portion of monochloramine increases and the chlorine required per unit weight of NH_3 -N oxidized should approach 7.6 parts, ignoring the chlorine demand resulting from other substances. However, further testing should be used to verify this conclusion in each individual case.

When accidental overdosing of chlorine has occurred or after an intentional addition of large quantities of chlorine to accelerate disinfection, it will be desirable to remove the excess chlorine. This is possible with a reducing agent, such as sulphur dioxide, sodium hydrogen sulphite or sodium thiosulphate:

$$SO_{2} + CI_{2} + 2H_{2}O + H_{2}SO_{4} + 2HCI$$
 (6.127)

$$NaHSO_3 + Cl_2 + H_2O + NaHSO_4 + 2HCl$$
 (6.128)
 $2Na_2S_2O_3 + Cl_2 + Na_2S_4O_6 + 2NaCl$ (6.129)

Oxidative degradation by chlorine is limited to a small number of compounds. Nevertheless, oxidation of these compounds contributes to overall reduction of BOD_5 in wastes treated with chlorine. A disadvantage is that chlorinated organic compounds may be formed in large quantities. A variety of chlorine compounds is applied in waste water treatments. For these compounds the available chlorine can be calculated. Generally this is expressed as percentage chlorine having the same oxidation ability. Data for the different chlorine-containing compounds are given in Table 6.43.

Table6.43Actualandavailablechlorineinpurechlorine-containingcompounds

Compound	Mol.	Chlorine equiv.	Actual chlorine	Available
	weight	(moles of Cl ₂)	(%)	chlorine (%)
$\begin{array}{c} Cl_2\\ Cl_2O\\ Cl_2O\\ ClO_2\\ NaOCI\\ CaCIOCI\\ CaCIOCI\\ Ca(OCI)_2\\ HOCI\\ NHCI_2\\ NH_2CI\\ \end{array}$	71 87 67.5 74.5 127 143 52.5 86 51.5	1 2.5 1 2 1 2 1 2 1 2	100 81.7 52.5 47.7 56 49.6 67.7 82.5 69	100 163.4 260 95.4 56 99.2 135.4 165 138

It can be seen that the actual chlorine percentage in chlorine dioxide is 52.5, but the available chlorine is 260%. This is, of course, due to the fact that the oxidation state of chlorine in chlorine dioxide is +4 which means that five electrons are transferred per chlorine atom, while Cl_2 only transfers one electron per chlorine atom.

Hypochlorite can be obtained by the reaction of chlorine with hydroxide in aqueous solution:

$$Cl_{p} + 2NaOH + NaCl + NaOCl + H_{p}O$$
 (6.130)

Chlorinated lime, also called bleaching powder is formed by reaction of chlorine with lime:

$$Ca(OH)_{2} + Cl_{2} \leftarrow CaCl(OCl) + H_{2}O \qquad (6.131)$$

A higher content of available chlorine is present in calcium hypochlorite, $Ca(OCI)_2$. Chlorine dioxide is generated in situ by the reaction of chlorine with sodium chlorite:

$$2NaClO_{2} + Cl_{2} + 2ClO_{2} + 2NaCl$$
 (6.132)

Theoretically, fluorine could be used for disinfection, but nothing is known about the bactericidal effectiveness of this element at low concentrations. However, bromine is used mainly for disinfection of swimming pools, the reason being **that monobromamine, unlike chloramine, is a strong bactericide.** There is therefore no need to proceed to breakpoint bromination. Bromine has a tendency to form compounds with organic matter, resulting in a high bromine demand. This and the higher cost are the major factors limiting the use of bromine for treatment of waste water.

lodine can also be used as a disinfectant. It dissolves sparingly in water unless iodide is present:

$$|^{-} + |_{2} - |_{3}^{-}$$
 (6.133)

It reacts similarly with water in accordance with the scheme for chlorine and bromine:

$$I_2 + H_2O - HOI + HI$$
 (6.134)

It has a number of advantages over chlorination. Iodine does not combine with the ammonium to form iodomines, but rather oxidizes the ammonia. Also it does not combine with organic matter very easily, e.g. it oxidizes phenol rather than forming iodo-phenols. However, iodine is costly and it has, up till now, found a use only for swimming pool disinfection.

Ozone is produced by passing compressed air through a commercial electric discharge ozone generator. From the generator the ozone travels through a gas washer and a coarse centred filter. A dispersion apparatus produces small bubbles with a large surface area exposed to the solution.

Ozone is used extensively in water treatment for disinfection and for removal of taste, odour, colour, iron and manganese, see also 6.4.4.

Ingols and Fetner (1957) have shown that the destruction of Escherichia coli cells with ozone is considerable more rapid than with chlorine when the initial ozone demand of water has been satisfied (see Fig. 6.66).

The activity of ozone is a problem in the disinfection of water containing high concentrations of organic matter or other oxidizable compounds. A

further problem arises from the fact that the decomposition of ozone in water does not permit long-term protection against pathogenic regrowth. *Hovever, ozone has the advantage of being effective against some chlorine-resistant pathogens, like certain virus forms* (Stumm, 1958).



Fig. 6.66. Disinfection of E. coli by chlorine and ozone (dosage mg/l).

The simultaneous removal of other compounds makes ozonation an advantageous water treatment process.

Ozone can be used to alleviate the toxic and oxygen demanding characteristics of waste water containing ammonia by converting the ammonia to nitrate.

The oxidation is a first order reaction with respect to the concentration of ammonia and is catalyzed by OH⁻ over the pH range 7-9. The average value of the reaction rate constant at pH 9.0 is $5.2 \pm 0.3 \cdot 10^{-2} \text{ min}^{-1}$. Ammonia competes for ozone with the dissolved organic constituents comprising the BOD and is oxidized preferentially relative to the refractory organic compounds, provided alkaline pH values can be maintained. Due to the elevated pH required, ammonia oxidation by ozone is attractive for the process of lime clarification and precipitation of phosphate.

The reaction of ozone with simple organic molecules has been exten-

sively studied in recent years.

The reactions are usually complex, subject to general and specific catalysts and yield a multitude of partially degraded products.

QUESTIONS.

- 1. Find the approximate BOD₅ for a waste water containing 120 mg l⁻¹ carbohydrates, 80 mg l⁻¹ proteins and 200 mg l⁻¹ fats.
- 2. Calculate the total oxygen demand (BOD₅ + nitrification) for domestic waste water with BOD₅ = 180 mg l⁻¹ and 38 mg l⁻¹ ammonium.
- 3. Write the chemical reaction for a denitrification of nitrate using acetic acid as a carbon source.
- Calculate BOD₁, BOD₂, BOD₁₀, and BOD₂₀ when BOD₅ = 200 mg l⁻¹ and the biological decomposition is considered to be a first order reaction.
- 5. Nitrification (99%) in a biological plant requires 6 hours retention time at 20°C. What retention time is necessary at 0°C?
- 6. Calculate the area necessary for spray irrigation of 100,000 m³ of waste water per year with a BOD₅ of 1000 mg l⁻¹. Maximum is 20,000 kg BOD₅ per ha per year and maximum application rate is 200-300 cm y⁻¹.
- 7. What disadvantages has the use of iron(III) chloride as a precipitant compared with calcium hydroxide and aluminium sulphate?
- 8. A waste water has a alkalinity corresponding to its hardness. It contains 120 mg l⁻¹ Ca²⁺ and 28 mg l⁻¹ Mg²⁺. How much calcium hydroxide should be used to adjust the pH to 11.0?
- 9. A waste water contains 6.5 mg P I^{-1} . How much 1) FeCl₃, 6H₂O, 2) Al₂(SO₄)₃, 18H₂O, must be used for chemical precipitation, when 90% P-removal is required?
- 10. A biological plant is designed to give 90% nitrification. The retention time and the aeration are sufficient, but the observed nitrification is only 80%. What should be done?

- Calculate the inhibition effect (as %) on the biological treatment of municipal waste water containing 2 mg l⁻¹ Hg²⁺ and 10 mg l⁻¹ Cu²⁺. The effects are considered to be additive.
- 12. Calculate the BOD₅ of a waste water that contains 25 mg l⁻¹ acetone, 20 mg l⁻¹ acetic acid, 10 mg l⁻¹ citric acid and 100 mg l⁻¹ glucose. What is the number of person eqv. of 150 m³ 24 hr⁻¹ is discharged?
- 13. Which of the following components can be treated on a mechanical-biological treatment plant (no adaptation is foreseen):
 1) Butyric acid, 2) 2,4-dichlorophenol, 3) polyvinyl-chloride, 4) pentanone, 5) stearic acid, 6) butadiene. Suggest a treatment method for each of the six components in the concentration range 10-100 mg l⁻¹.
- 14. What is the minimum cost of activated carbon (US\$ 0.40 per kg) for the treatment of 1 m³ of waste water containing: a) 25 mg l⁻¹ chloro-benzene, b) 10 mg l⁻¹ toluene, c) 52 mg l⁻¹ dodecylbenzene sulphonate?
- 15. Suggest a treatment method for waste water containing diethyldisulphide.
- 16. How much Ni^{2+} remains in industrial waste water after precipitation with calcium hydroxide at pH = 9.5? What methods are available if a concentration of 0.005 mg l⁻¹ or less is required?
- Calculate the stoichiometrical consumption of chemicals for treatment of 100 m³ 24 hr⁻¹ of waste water containing 120 mg l⁻¹ Cr₂O₇²⁻. A reduction to Cr³⁺ using Na₂SO₃ + HCl precipitation with calcium hydroxide is suggested.
- 18. Indicate how 2 g $|^{-1}$ Cu²⁺, 4 g $|^{-1}$ Zn²⁺ and 1 g $|^{-1}$ Mn²⁺ can be separated by extraction.
- How much 1) chlorine, 2) ozone, 3) NHCl₂, 4) ClO₂ is required to give a 99.9% desinfection of E. coli, provided that no oxidation of organic matter takes place? (Contact time 15 min. at pH 8.5).
- 20. Which has the highest disinfection effect: 1 mg l⁻¹ chlorine at pH 7.2 at 10°C, or 1.2 mg l⁻¹ chlorine at pH 7.8 at 20°C?
- 21. Design an aerated pond (5 steps are considered) for treatment of 250 m³

 d^{-1} waste water from an aquaculture plant. The ponds should bring the BOD₅ from 80 mg l⁻¹ to 10 mg l⁻¹. How much oxygen must be supplied to the ponds?

- 22. A lake has a catchment area of 50 ha. It covers an area of 12 km² and has an average depth of 15 m. Annual precipitation is 600 mm. Set up an approximate N- and P-balance for the lake, when it is known that a waste-water plant with mechanical-biological treatment discharges 2000 m³ d⁻¹ to the lake. Characterize the eutrophication of the lake and consider what improvement one should expect after 90% removal of P or N from the waste water.
- 23. Design an activated-sludge reactor and determine the weight of waste sludge per unit of time for treatment of 25,000 m³ d⁻¹. k_d and a are determined by pilot-plant experiments to be 2.5 and 0.8 d⁻¹. BOD₅ of the influent is 180 mg l⁻¹ and an effluent of BOD₅ = 12-15 mg l⁻¹ should be obtained.
- 24. Design a plastic trickling filter for the same problem as given in 23. Use 3 parallel filters with a depth of 7 m. The temperature varies from 14°C to 24°C. Try to recycle 2 and 3 times and comment on a comparison of the 2 results. $k = 0.08 \text{ min}^{-1}$ at 20°C.