ScorePP

Priority pollutant behaviour in on-site treatment systems for industrial wastewater

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Mike Revitt, Lian Scholes and Erica Donner
 Urban Pollution Research Centre, Middlesex University, UK.

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Authors:	Mike Revitt, Lian Scholes and Erica Donner
Review and Assessment	Natasa Atanasova, University of Ljubljana
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Abstract

The identified deliverable for this task is a 'Database of non-substitutable industrial priority pollutants (PPs) and appropriate on-site reductions'. The considered PPs are consistent with those which were previously allocated emission strings, see Task 3.2.

Conventional industrial treatment techniques are described according to the nature of the process (e.g. separation/clarification) and also with reference to their application to PP characteristics (e.g. suspended solids and insoluble liquids). In each category, information is provided on the scientific principles involved, on the equipment and process details, and, when available, the PP removal efficiencies or achievable effluent levels are given. The relative advantages compared to other techniques are described as well as how the different techniques might be combined. Industrial treatment techniques were each assigned a treatment code and, where possible, they relate to a particular production process either as a single technique or as a combination of techniques. Sometimes, generic treatment options are described for either a PP or a group of PPs.

The combination of the descriptions of different industrial treatment technologies and the database on classification and treatment efficiencies provides a comprehensive overview of the current state of practice with regard to the industrial control of PPs in process waters.

Acknowledgement

PART A: CONVENTIONAL TREATMENT TECHNIQUES FOR PRIORITY POLLUTANTS GENERATED BY INDUSTRIAL PROCESSES

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PART B: DATABASES FOR INDIVIDUAL PRIORITY POLLUTANTS IDENTIFYING APPLICABLE TREATMENT PROCESSES AND REMOVAL EFFICIENCIES/ACHIEVABLE EMISSION LEVELS.

PART A: CONVENTIONAL TREATMENT TECHNIQUES FOR PRIORITY POLLUTANTS GENERATED BY INDUSTRIAL PROCESSES

This part of the deliverable is designed to be used in conjunction with the database which is contained in Part B of this Deliverable. The referencing systems used within the database and this part of the document (Part A) enable the user of the database to obtain additional relevant information relating to the conventional treatment techniques which are available for the removal of pollutants from industrially generated wastewaters. In addition, Part A provides a general introduction into the processes leading to the production of wastewaters by the chemical industry.

1. Production of wastewaters by the Chemical Industry

The majority of wastewaters deriving from the chemical industry consist of aqueous discharges produced during the physico-chemical processing of synthetic mixtures involving operations such as filtration, centrifugation, extraction and/or distillation. The wastewater streams, referred to as 'process waters' can include mother liquors, washing waters from the purification of products, vapour condensates, quench waters, wastewaters from exhaust air/flue gas clean-up, wastewaters from equipment cleaning and wastewaters from vacuum generation. Consequently industrial wastewaters can contain a range of contaminants representing the compounds involved at each stage of the chemical process e.g. unreacted starting materials, intermediate compounds, unwanted by-products etc which often constitute the poorly biodegradable content of the total wastewater load. Where organic solvents have been used they often contribute substantially to the organic pollutant load reaching the wastewater treatment facility

Additional wastewater streams requiring treatment can be generated from other on-site sources such as scrubbing of exhaust gases from incineration and combustion, bleed from boiler feed water systems, back-washing of filters, laboratory and pilot-scale plants and collection of rainwater from contaminated areas.

Because of their complex nature, the environmental impacts of industrial wastewater streams are not, normally definable by their loads or concentrations. For example, the impact of hazardous and toxic contaminants with concentrations close to the detection limit can be significant in contrast to high concentrations of non-toxic substances. In addition to toxic effects occurring in individual streams from chemical industries, those not showing toxic effects may interact synergistically when mixed together either in the sewerage system or in the receiving water.

2. Handling procedures for Chemical Industry wastewaters

Preferentially, the wastewater stream arising directly from a process should be treated to reduce its pollutant content at an early stage. In practice, this is only feasible in newly built plants due to the high capital costs or retrofitting limitations (e.g. lack of space) associated with existing ones. Therefore, the chemical industry like most other industrial sectors resorts to end-of-pipe treatment techniques to reduce wastewater pollutant loads. This can involve pre-treatment or final treatment of separated wastewater streams as well as the central treatment of collected wastewater before discharge into receiving waters.

Different systems exist for the collection and treatment of chemical process waters. Decentralised wastewater treatment facilities are designed to treat aqueous effluents at source and discharge them directly into receiving waters. This is the preferred option when there are tributary wastewater streams which exhibit completely different properties and which therefore would respond differently to different treatment options. There are a number of advantages of using decentralised wastewater treatment systems or treatment at source. Because such systems are usually specifically designed they are more likely to show better performance (particularly when non-biological techniques, which are independent of the biodegradability of wastewater streams, are used) which is assisted by the local operators having full responsibility for the quality of their own wastewater discharge. The treatment efficiency is also enhanced by the avoidance of dilution effects arising from the mixing of different wastewater streams. There is more flexibility for change and enlargement within the works environment and improved cost benefit ratios can be achieved. Where the alternative would be to use a central biological treatment there will be reductions in the amount of excess activated sludge requiring disposal.

Centralised wastewater treatment typically involves the use of a central Wastewater Treatment Plant (WWTP) which receives all contaminated discharges or which is preceded by some upstream pre-treatment at source. These systems often involve biological treatment. A specific advantage of a centralised WWTP is that where a tributary stream has poor biodegradability, synergistic effects created by mixing with biodegradable wastewaters can lead to the microbiological degradation of otherwise inert contaminants. Such mixing effects can also be beneficial in terms of temperature or pH adjustment. Central treatment plants can make more effective use of chemicals (e.g. nutrients) and equipment, thus resulting in decreased operating costs.

A third overall treatment option is to direct the wastewater from the industrial site to a municipal WWTP either with or without on-site pre-treatment at source. In some instances the WWTP is specially built for the combined treatment of municipal and chemical industry wastewater. Such joint treatment facilities are often designed so that the industrial wastewater (because of its high initial organic loading and tendency to decreasing degradation rates in diluted wastewater) initially undergoes a high performance (high load) treatment stage, and is subsequently joined by the municipal wastewater in a second biological (low load) treatment step. An advantage of combined

industrial/municipal wastewater treatment is a saving in capital and operating costs. The operational stability of joint biological treatment can be favourably influenced by a number of factors. These include the opportunity to improve the nutrient conditions and to optimise the wastewater temperature and thus the degradation kinetics. It is important that the toxic and inhibitory effects of industrial wastewater constituents are lowered below critical concentration thresholds. There is a particular danger of hindering the nitrification process, necessitating careful monitoring of the wastewater streams coming from the industrial plant. There is the possibility that persistent pollutants, such as heavy metals and non-biodegradable organic compounds, may avoid treatment and be discharged into receiving waters or become concentrated in sludge making it too contaminated for further use or treatment. Ideally, the industrial site should have a separate sewer system for the collection of uncontaminated rainwater and cooling water to avoid hydraulic overload problems at the WWTP during periods of heavy rainfall possibly leading to increased pollutant discharges and damage to the activated sludge.

3. Treatment techniques for Chemical Industry wastewaters

The treatment methods employed to treat contaminated wastewaters originating from industrial chemical sites are based on physical, chemical or biological processes or suitable combinations of these. Separation or clarification techniques are examples of physical processes which are commonly used as the first stage of a treatment system (to protect subsequent treatment stages against damage, clogging or fouling by solids) or as a final clarification step (to remove solids or oil formed during a preceding treatment operation). Examples of these techniques are identified in Table 3.1.

The wide range of physico-chemical treatment processes (Table 3.1) are typically applied to non-biodegradable wastewaters containing, for example, inorganic or poorly biodegradable organic pollutants. These techniques are widely used as pre-treatment steps upstream of a central wastewater treatment plant. This will typically utilise biological treatment, which may focus on aerobic digestion processes, anaerobic digestion processes or nitrification/denitrification processes.

Table 3-1 Examples of treatment techniques categorised according to scientific process

Treatment process	Examples
Separation/clarification	grit separation; sedimentation ; air flotation; filtration; microfiltration/ultrafiltration; oil-water separation.
Physico-chemical treatment	precipitation/sedimentation/filtration ; crystallisation; chemical oxidation; wet air oxidation; super-critical water oxidation; chemical reduction; hydrolysis; nanofiltration / reverse osmosis; adsorption; ion exchange; extraction; distillation/rectification; evaporation; stripping; incineration.
Biological treatment	anaerobic digestion processes: e.g. anaerobic contact process, UASB process, fixedbed process, expanded-bed process, biological removal of sulphur compounds and heavy metals. aerobic digestion processes: e.g. complete-mix activated sludge process, membrane bioreactor process, trickling filter process, expanded-bed process, biofilter fixed-bed process. nitrification/denitrification

4. Treatment techniques appropriate to different pollutant groups

In this section, the treatment techniques which are most relevant to different groups of commonly occurring pollutants are discussed. Where appropriate (i.e. where relevant specific treatment information exists) priority pollutants are associated with the identified treatment techniques and reference made to Section B3 where additional detail can be found.

4.1 Oil and/or hydrocarbons

Individual or combinations of treatment systems should be employed to produce a treated effluent with a total hydrocarbon concentration not exceeding the range of 0.05-1.5 mg/l, expressed as a monthly average. In the case of heavy oil pollution, which can interfere with other components of the waste system, recovery can be maximised by applying an appropriate combination of oil/water separation by cyclone, microfiltration or API (American Petroleum Institute) separator (e.g. benzene [B3.3]). For less severe oil pollution incidents, parallel plate or corrugated plate interceptors can be used. Additional treatment techniques include granular media filtration, gas flotation or biological treatment.

4.2 Suspended solids (TSS)

Suspended solids can cause damage or failure to downstream facilities and therefore ideally need to be removed at an early stage in the overall treatment process. Sedimentation/air flotation processes are appropriate for removal of the main TSS load with mechanical filtration being suitable for further solids reduction. Where a solid-free effluent is required before discharge into a receiving water, microfiltration or ultrafiltration are preferred techniques.

4.3. Heavy metals

Heavy metals cannot be destroyed and therefore recovery and re-use are used to prevent them being released into the environment. Under Best Available Technology (BAT) the approach should involve a series of steps involving the initial segregation of the wastewater containing heavy metal compounds and treatment before mixing occurs with other streams. Appropriate recovery techniques for heavy metals include precipitation/sedimentation (e.g. cadmium [B3.5]; lead [B3.17]; mercury [B3.18]; nickel [B3.19]) (or air flotation) followed by filtration (e.g. nickel [B3.19]) (or microfiltration or ultrafiltration); crystallisation; ion exchange (e.g. cadmium [B3.5]; mercury [B3.18]) or nanofiltration (or reverse osmosis).

Heavy metal removal may also be included as part of a final polishing step in a WWTP, with subsequent treatment of sludge, if necessary. The discharge levels that can be achieved by the identified control techniques are strongly dependent on the source processes releasing the heavy metals, and therefore the identification of emission levels that are valid for the chemical sector as a whole have not yet been identified.

4.4. Inorganic salts (and/or acids)

The removal of these constituents from wastewaters is necessary to ensure efficient operation of sewerage system by limiting the corrosion of pipes, valves and pumps and preventing potential damage to a downstream biological treatment system. The discharge of high salt loads to a receiving water can have a deleterious effect on the ecology. Therefore, it is considered good practice to control the inorganic salt content at source and preferably with control techniques that enable recovery. Appropriate treatment techniques are evaporation, ion exchange and reverse osmosis. A specific treatment technique for sulphates is biological sulphate removal which will also remove any heavy metals which may be present.

4.5. Pollutants unsuitable for biological treatment

In order to maintain the efficient functioning of the microbial communities in a biological treatment plant it is necessary to prevent the entry of both toxic substances and recalcitrant organic compounds. It is advisable to restrict all waste water components which it is considered will inhibit the biological process as this cannot be accurately predicted due to the different adaptation characteristics of the microorganisms operating in a specific plant. If substance recovery is required, the possible techniques for removal of non-biodegradable components are nanofiltration (e.g. atrazine [B3.2]) or reverse osmosis (e.g. chlorpyrifos [B3.7]), adsorption (e.g. atrazine [B3.2]; chloroalkanes [B3.6]; chlorpyrifos [B3.7]; diuron [B3.10]), extraction, distillation/rectification, evaporation and stripping (e.g. benzene [B3.3]; chloroalkanes [B3.6]; ethylene dichloride [B3.13]; hexachlorobenzene [B3.14]; hexachlorobutadiene [B3.15]; pentachlorobenzene [B3.22]). When recovery is not an option but energy needs to be conserved, chemical processes such as oxidation, reduction or hydrolysis are appropriate. The extreme techniques, involving considerable energy consumption, for reducing toxicity or inhibitory effects are wet air oxidation (e.g. benzene [B3.3]) or wastewater incineration

4.6. Biodegradable contaminants

Biological treatment systems may be located at different stages in an overall treatment facility. The use of a central biological wastewater plant to treat mixed wastewaters has already been discussed. The objective for the effluent from such a system should be a BOD not exceeding 20 mg/l. If an activated sludge process is being used, a typical application is a low-loaded biological stage with a daily COD load of ≤ 0.25 kg/kg sludge.

Wastewaters which are heavily contaminated with biodegradable components may require pre-treatment at source using either anaerobic or aerobic (e.g. benzo(a)pyrene [B3.4]; hexachlorobenzene [B3.14]; hexachlorobutadiene [B3.15]; pentachlorobenzene [B3.22]) high load systems. Biological systems can also be used as a final polishing step after a central wastewater treatment plant and examples of suitable processes for this and pre-treatment are the anaerobic contact process, the upflow anaerobic sludge blanket process, the anaerobic and aerobic fixed-bed process, the anaerobic expanded-bed process, the complete-mix activated sludge process, membrane bioreactors,

trickling (percolating) filters and the biofilter fixed-bed process. If the waste water contains a high nitrogen load, nitrification/denitrification processes may be used.

A simplified diagram showing the typical order in which the different treatment processes are likely to be found in an industrial site is shown in Figure 4.1. This is not accurate for all chemical industry applications but serves as a general guide to the relative locations of the various techniques. The arrows linking the different processes have been kept to a minimum to reduce complexity although, in practice, there can be many more inter-connections between the different boxes. The processes identified under sludge treatment are not discussed in any detail here as they will be considered in Deliverable 5.5. Each of the wastewater removal processes is described in more detail in the following sections.

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┌──────────────────────────────────┐
│      Contaminated wastewater      │
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┌──────────────────────────────┐
│      Sludge treatment        │
│         Thickening           │
│         Dewatering           │
│        Stabilisation         │
│        Conditioning          │
│      Thermal reduction       │
└──────────────────────────────┘
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┌──────────────────────────────────┐
│     Suspended solids and          │
│      insoluble liquids            │
│        Grit separation            │
│     Sedimentation (including      │
│     coagulation/flocculation)     │
│         Air flotation             │
│          Filtration               │
│   Membrane filtration (MF, UF)    │
│      Oil-water separation         │
└──────────────────────────────────┘
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┌──────────────────────────────┐
│       Inorganic/non-         │
│   biodegradable/poorly       │
│    biodegradable soluble     │
│         pollutants           │
│        Precipitation         │
│        Crystallisation       │
│      Chemical oxidation      │
│       Wet air oxidation      │
│  Supercritical water oxidation│
│      Chemical reduction      │
│      Chemical hydrolysis     │
│  Nanofiltration/Reverse osmosis│
│          Adsorption          │
│        Ion exchange          │
│         Extraction           │
│    Distillation/rectification│
│         Evaporation          │
│          Stripping           │
│         Incineration         │
└──────────────────────────────┘
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┌──────────────────────────────┐
│  Biodegradable soluble       │
│       pollutants             │
│    Anaerobic treatment       │
│  Anaerobic contact process   │
│        UASB process          │
│  Fixed bed (or filter) process│
│     Expanded bed process     │
│   Biological removal of      │
│     sulphur and metals       │
│ Complete mix activated sludge │
│          process             │
│  Trickling (percolating) filter│
│          process             │
│     Expanded bed process     │
│   Biofilter fixed-bed process│
│   Biological nitrogen        │
│       elimination            │
└──────────────────────────────┘
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┌──────────────────────────────┐
│        Receiving water       │
└──────────────────────────────┘
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Figure 4-1 Flow diagram showing the inter-relationships between different pollutant removal processes in a typical chemical industry wastewater treatment scheme.

5. Descriptions of the treatment processes for suspended solids and insoluble liquids

In addition to general descriptions of the individual processes, this section also comments on the relative advantages and disadvantages and, where possible, examines the performance capability of the process.

5.1. Grit Separation

The separation of grit is not specifically for environmental protection but to ensure that downstream equipment (e.g. pumps) is not damaged and that there is no interference with subsequent treatment processes. It is normally required when a treatment plant receives stormwater as this can entrain substantial amounts of sand. Grit chambers are typically designed to deal with horizontal flow rates of around 0.3 m/s under which conditions sand is separated and the lighter solids are transported in the ongoing wastewater stream.

5.2. Settling/sedimentation/clarification

These processes involve the separation of suspended particles and floating material by gravitational settling. The settled solids are removed as sludge whereas remaining floating material is skimmed from the water surface. For those particles which do not separate efficiently under gravity due to their size, density or colloidal nature, the separation process can be assisted by flocculation/coagulation. The addition of coagulants, such as aluminium sulphate (alum), ferric sulphate and chloride, lime, poly aluminium chloride, and cationic organic polymers, under controlled pH conditions, cause the destabilisation of colloidal and small suspended particles and emulsions enabling them to form flocs which are large enough to settle under gravity. The addition of anionic and non-ionic polymers assists the flocculation process. It is important to note that the floc may incorporate other contaminants that could lead to problems in the subsequent disposal of the sludge.

The equipment for coagulation and flocculation precedes the settling tank and needs to initially allow rapid mixing for the coagulation process followed by gentle stirring in a mixing chamber to encourage flocculation. Sedimentation is achieved by using:
- rectangular or circular flat tanks, equipped with a scraper and of an appropriate size to provide a settling residence time of about 1.5 to 2.5 hours
- hopper-bottom tanks, with vertical flow, usually not equipped with a mechanical sludge removal system
- lamina or tube settlers, using plates to enlarge the sedimentation surface

To ensure optimum settling conditions, an upstream oil separation or emulsion decomposition stage is normally installed to remove interfering substances.

Sedimentation is a widely used separation technique for many purposes. It can be used individually such as for the removal of inert materials, such as sand, from process wastewater or collected rainwater. It is also used in conjunction with other techniques,

such as the removal of polymers and their monomers following the addition of appropriate chemicals. Heavy metals and other dissolved components may be removed by settling after preceding precipitation followed by a final filtration process. Clarification is also widely practised to remove activated sludge following primary or secondary biological treatment in a WWTP. The sedimentation process is not recommended in the presence of volatile substances which can be released during the long residence times in the settling tank as well as being enhanced by the mixing action involved in coagulation and flocculation processes.

Sedimentation can remove between 60 and 90% of total suspended solids (TSS) increasing to 90 to 95% for settleable solids. Where the TSS includes a considerable amount of particulate organics, sedimentation will therefore reduce the TOC/COD content substantially. The emission level of TSS, after the final clarification of a central WWTP, should be below 10 mg/l.

5.3. Air Flotation

Flotation is a process whereby suspended matter, such as oils or solids, is separated from the wastewater phase through attachment to air bubbles. The buoyant particles accumulate at the water surface where they can be removed by a skimming device (Metcalf and Eddy Inc, 1991). Flocculant additives, such as aluminium and ferric salts, and various organic polymers, can be introduced to support the flotation process by providing a surface or structure which is able to absorb or entrap the air bubbles. Flotation is the most widely used approach to solid-liquid separation in decentralised wastewater treatment and has considerably lower costs than evaporation or incineration (typically by a factor of approximately 10). However, the environmental benefits of evaporation and incineration are greater, as they can completely dispose of a highly contaminated effluent, whereas the flotation processes achieves only partial treatment of a moderately contaminated split stream.

There are different methods of flotation, depending on the method of air bubble introduction. In vacuum flotation, the air is dissolved at atmospheric pressure, and a subsequent pressure drop allows the formation of bubbles. The process involving the drawing of fine bubbles into the wastewater via an induction device (venturi or orifice plate) is known as induced air flotation (IAF). A widely used technique is dissolved air flotation (DAF), in which air is dissolved in wastewater under pressure and then released at atmospheric pressure in a flotation tank or basin. The released air forms tiny bubbles which adhere to the suspended matter enabling it to float to the surface (Beychok, 1967; Wang *et.al.*, 2004; Kiuru and Vahala, 2000).

A schematic diagram showing the components within a typical DAF unit is shown in Figure 5.1. Following treatment, a small portion of the clarified effluent leaving the DAF tank is pumped into a small pressure vessel (called the air drum) into which compressed air is also introduced. The resulting air-saturated water stream is directed to the front of the floatation tank and where it passes through a pressure reduction valve. This causes the release of fine air bubbles which transport any suspended matter to the surface. The froth layer is skimmed off allowing froth-free effluent to leave the DAF tank.

In some DAF units, parallel plate packing materials are included to increase the separation surface and therefore to enhance the overall efficiency.
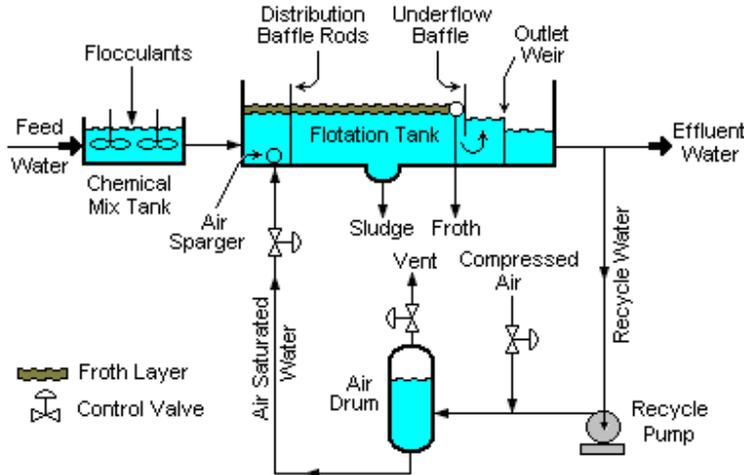
Figure 5-1 The components of a typical dissolved air flotation unit (DAF)

Flotation tends to be applied when sedimentation is not appropriate due to poor particulate settling characteristics, lack of a sufficient density difference between the suspended particles and the wastewater, or oil and grease need to be removed. It is widely used in refineries and petrochemical facilities as a subsequent treatment downstream of oil separation and prior to a biological WWTP. Other direct industrial uses include the removal of dyes and pigments from production wastewaters, the recovery of products or raw materials (e.g. toluene from toluene/water emulsions) and the separation of heavy metals from wastewaters. It can also be used for the separation of activated sludge from biologically treated wastewater and the thickening of activated sludge from a biological WWTP.

In comparison to sedimentation, flotation requires less space (equipment size) and therefore involves lower capital costs. It maintains a high separation efficiency with progressively increasing hydraulic loading rates and the separated material has a higher dry matter content compared to sedimentation. Disadvantages are that the clogging of valves is possible and because of the high potential for odour release, covering of the treatment unit is normally required. The separation of wastewaters containing foaming detergents is not feasible and there are higher operational costs compared to sedimentation.

Quoted removal efficiencies for TSS are between 85 and 98% with emission levels of 10 to 20 mg/l (Biener et.al., 1999). For oils, a similar emission value is reported following the use of IAF and DAF techniques (Dutch Ministry of Housing, Spatial Planning and the Environment, 1999). TOC/COD will be proportionately removed/emitted according to their content within the suspended solids or liquids.

5.4. Filtration

Very fine solids and solids with densities close to the density of water which cannot be directly removed by sedimentation techniques can be separated from the aqueous phase by filtration. Filtration is the process by which solids are removed by passing the wastewater effluent through a porous medium. Sand is widely used as a filtration medium for wastewaters with low solids content. The wastewater can be directed through the granular-medium filter bed by either downward or upward flow and either under gravity or an applied pressure. The filtration process can be semi-continuous in which filtration and backwashing occur sequentially and the filtration is continued until turbidity breakthrough occurs (due to increasing solid content in the effluent) due to limiting head loss. The backwashed material is normally re-circulated to the process from where it originated, e.g. to the sedimentation tank or the activated sludge basin of a biological WWTP. Figure 5.2 shows a schematic diagram of a multi-media sand filter operating under gravity flow.
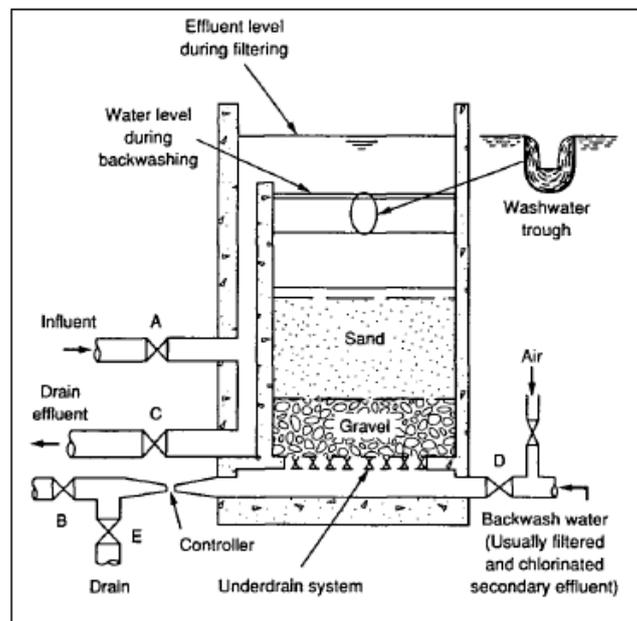
Figure 5-2 Schematic diagram of a conventional down-flow multi-media sand filter.

Drum filters utilise a fabric wrapped around a cylinder to achieve filtration. They can be operated under gravity with the effluent directed to either the inside or the outside of the drum or as rotary vacuum filters with one side of the drum enclosed and connected to a vacuum pump. They are commonly used for sewage treatment and removal of activated sludge flocs. Sludge de-watering can be achieved using a rotary vacuum filter or belt filter press. The latter can also be used for liquid/solid separation operations where there is a high solids content. As for sand filters, these 'cake' filters require cleaning at some stage in their use to maintain efficiency. Cake filters require more frequent backwashing than the deep bed filtration associated with sand filters and therefore these systems tend to be used less often in wastewater treatment. The residue from these filters can either be recycled or has to be discharged of as waste or undergo further treatment. Membrane filters are discussed in a separate section of this report.

There are a number of important characteristics which need to be carefully considered when selecting the filter media. The permeability influences the filtration rate with high permeabilities being characterised by low pressure drops. The mechanical strength of the filter media needs to be considered with respect to the loads imposed during back-blowing or the movement of filter cloths. The blocking tendency, particularly for fabrics in cake filtration, needs consideration as does the contribution of a smooth surface for promoting cake removal. It is important that the filter media is chemically stable with respect to the filtrate. The pore size (where applicable) is often used to select the filtering capability of a filter medium but more relevant is the cut-off size, as this defines the particle size that can just pass through the filter medium.

The filtering of suspensions composed of fine, soft or compressible solids can be difficult because of their tendency to fill or block the filter medium. This can be prevented by using filter aids (inert, readily filterable granular material) to pre-coat the filter medium before filtration starts. The filter aid layer is permeable to the filtrate and the retained particles are deposited on top of it. It is normal practice to continuously add the filter aid to the slurry during filtration to maintain the required ratio for efficient filtration. Filter aids include substances such as diatomaceous earths, powdered glass, cellulose fibres, talc and plastics.

Filtration is frequently used as the final separation stage in wastewater treatment (e.g. after sedimentation or flotation) when low emissions of particulates are required. Examples are the separation of flocs after sedimentation, to cope with discharge requirements and the removal of activated sludge after a central WWTP to improve the quality of biologically treated wastewater effluent. Filtration systems are capable of achieving high separation efficiencies but cannot be used for colloids or emulsions without additional chemical treatment. They can operate under a wide range of conditions but breakthrough is always possible leading to pollution of the effluent.

The reported performance efficiency of sand filters for TSS is between 50 and 99.99% depending on the use of filter aids. The achievable emission levels are less than 10 mg/l for TSS as an activated sludge floc and below 5 mg/l for free oil. Heavy metals can be removed by filtration following precipitation which is discussed in Section 6.1.

5.5.   Microfiltration and ultrafiltration

These are filtration processes which remove contaminants from wastewater by passage of the permeate through a microporous membrane leaving behind the concentrate, which is retained. The driving force for the process is the pressure difference across the membrane. A typical microfiltration (MF) membrane pore size range is 0.1 to 10 µm and for ultrafiltration (UF), the pore size range is 0.001 to 0.1 µm. Solvents and particles of molecular size can pass through the pores, whereas suspended particles, colloidal particles, bacteria, viruses, and even larger macromolecules are held back. Other characteristics of the two techniques are identified in Table 5.1.

Table 5-1 Typical characteristics of microfiltration and ultrafiltration membrane filters.

Parameter	Microfiltration	Ultrafiltration
Pore diameter (µm)	0.1-1 0	0.001–0.1
Operating pressure (MPa)	0.02–0.5	0.2–1
Cut-off size (nm)	>100, includes bacteria	10-100, includes macromolecules, viruses, colloidal particles 1000–100000 g/mol for solutions
Permeate flow ($l\ m^{-2}\ h^{-1}$)	50–1000	<100
Cross flow speed [m/s]	2-6	1-6
Membrane type	symmetrical polymeric or ceramic, 10–150 µm thick	polymeric, or ceramic asymmetric
Membrane configuration	spiral-wound hollow-fibre tubular	spiral-wound hollow-fibre tubular

(Environment Agency (UK), 1997; Ullmann's Encyclopedia of Industrial Chemistry, 2000; Entec UK Ltd., 1997).

The membrane filtration process is usually operated in a cross-flow configuration such that the permeate flow is directed perpendicular to the feed flow. The impurities remain in the feed and typically the concentrated waste stream is approximately 10 % of the original feed volume. The removed target substances attain approximately 10 times their concentration in the original feed and it is therefore important to assess the disposal options for this residue. When this consists of organic suspended substances, the concentration increase might improve the conditions for subsequent oxidative destruction processes. For inorganic suspended substances, the concentration stage could be used as part of a recovery process. In both cases, the permeate water from a membrane process can potentially be re-used or recycled in the industrial process, thus reducing both water input and discharge.

Membranes for MF and UF are available in several materials and configurations. The optimum modification for a particular application will depend on the nature of the wastewater, since the different membrane materials have varying resistances to dissolved substances. Typical membrane materials for MF are glass fibre, polycarbonate, PVDF (polyvinylidene fluoride), cellulose acetate and polyamide. Suitable materials for UF are normally organic polymers such as cellulose acetate, polyamide, polyimide, polycarbonate, polyvinylchloride, polysulphone, polyethersulphone, polyacetal, copolymers of acrylonitrile and vinyl chloride, polyelectrolyte complexes and cross-linked polyvinyl alcohol or polyacrylates. PVDF membranes have the advantage that they can be cleaned with strong acids, caustic soda and bleaches.

Microfiltration and ultrafiltration are applied when a solid-free wastewater is needed for downstream facilities (e.g. reverse osmosis) or the complete removal of hazardous contaminants such as a heavy metals or toxic organic compounds is required. The choice between MF and UF is dependent on the particle size removal range needed (see Table 5.1). Common MF applications include oil-water separations and degreasing processes, metal removal/recovery, metal plating waste water treatment, and sludge separation after the activated sludge process in a central biological WWTP. Common UF applications include removal of non-toxic degradable pollutants such as

proteins and other macromolecular compounds and toxic non-degradable components (e.g. dyes and paints) with molecular weights greater than 1000. In addition, UF is used for the segregation of oil/water emulsions and the separation of heavy metals following complexation or precipitation. UF can separate those components which are not readily degradable in sewage treatment effluents and which are subsequently recycled to the biological stage.

Membrane filtration systems offer high separation efficiencies and can achieve removal efficiencies consistently close to 100% and emission levels approaching zero for TSS. They are available as modular systems which offer flexibility in their usage. However, clogging, plugging and fouling processes can reduce their efficiency. They have limited mechanical stability and because they operate at high pressures, they require high pumping energy. The pressure levels are set to maintain a minimum velocity of about 2 m/s across the membrane surface.

5.6.   Oil-water separation

The methodologies used for the separation of oil and water and the subsequent removal of the separated oil depend on the nature of the oil contamination. Where free oil exists, gravity separation can be applied using specialised separation equipment. If an emulsion exists, emulsion breaking chemicals (e.g. polyvalent metal salts [alum, ferrous chloride], mineral acids [sulphuric, hydrochloric or nitric acid], adsorbents [pulverised clay] or organic polymers [polyacrylates]) need to be added and the de-emulsified oil separated by coagulation/flocculation and air flotation (see Section 5.3).

The API oil-water separator is a device designed to separate large amounts of oil (and also suspended solids) from wastewaters. The principle of Stokes Law is applied to define the rise velocity of oil droplets based on their density and size. It is designed according to standards published by the American Petroleum Institute (API) (American Petroleum Institute (API), 1990; Beychok, 1967) and utilises the fact that the difference in specific gravity between the oil and the wastewater is much smaller than the specific gravity difference between the suspended solids and water. Hence, most of the suspended solids will settle to the bottom of the separator as a sediment layer whereas the oil will rise to the top with the wastewater representing the middle layer. A schematic diagram of a typical API oil-water separator is shown in Figure 5.3. The oil layer is skimmed off and subsequently re-processed or disposed of, and the bottom sediment layer is removed by a scraper and a sludge pump. The water layer may be sent for further treatment consisting of a dissolved air flotation (DAF) unit (see Section 5.3) for further removal of any residual oil and then to a biological treatment unit for the removal of undesirable dissolved chemical compounds.

1 Trash trap (inclined rods)
2 Oil retention baffles
3 Flow distributors (vertical rods)
4 Oil layer
5 Slotted pipe skimmer
6 Adjustable overflow weir
7 Sludge sump
8 Chain and flight scraper
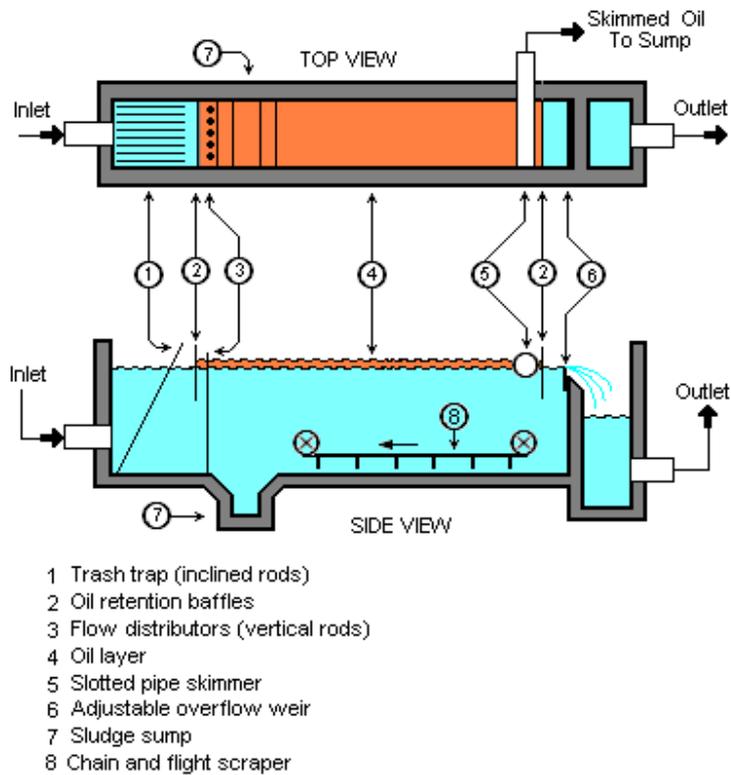
Figure 5-3 Top and side views of a typical API oil-water separator.

An alternative design involves parallel plate separators which are similar to API separators but include tilted parallel plate assemblies (parallel packs). The underside of each parallel plate provides more surface area for suspended oil droplets to coalesce into larger globules and provides a greater efficiency than API separators for the removal of smaller oil droplets. Any sediment slides down the topside of each parallel plate. Parallel plate interceptors (PPI) still depend upon the specific gravity between the suspended oil and the water but the parallel plates enhance the degree of oil-water separation. The result is that a parallel plate separator requires significantly less space than a conventional API separator to achieve the same degree of separation. A revised version of the PPI involves the use of corrugated plate packs placed in a counter current flow direction. This system, known as the Corrugated Plate Interceptor (CPI), is represented in Figure 5.4.
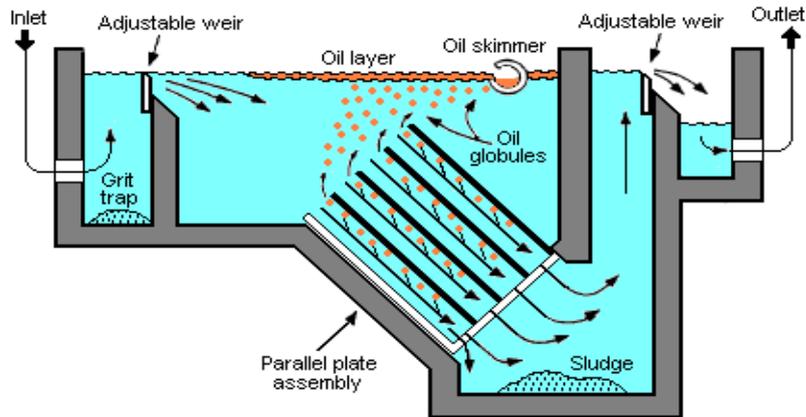
Figure 5-4 A representation of a corrugated plate oil-water separator (PPI)

Oil-water separation is applied to remove oil, grease and other non-soluble liquids lighter than the aqueous phase from wastewater, mainly in refineries and petrochemical sites. The API system can be used as a control device to protect downstream equipment against large oil slugs, originating e.g. from an operational failure. In the case of PPI and CPI systems, the plates are susceptible to fouling and leading to an increased maintenance requirement. Oil-water separators, when not covered, are the main contributors to VOC releases in wastewater treatment systems of which they are part and thus represent a major odour and health risk. Surface covering can reduce VOC release by about 95 % (CONCAWE, 1999) but appropriate ducting of the waste gas needs to an abatement system is necessary.

The performance efficiencies of these separators are between 90 and 95% for both oil and suspended solids. The emission levels quoted for the API separator are 6 to 90 mg/l for oil refinery application and 40 to 70 mg/l (ENTEC UK Ltd., 1996) when used in the chemical industry. It is clear from these fairly elevated emission levels why further treatment is often required.

6. Description of the treatment processes for inorganic/non-biodegradable/poorly biodegradable soluble pollutants

The wastewater contaminants discussed in this Section include inorganic compounds (salts or heavy metal compounds), organic compounds (contributing to refractory TOC) and inhibitory organic or inorganic compounds that are likely to disturb the biological processes in a WWTP. These substances require pre-treatment upstream of a central WWTP by options such as chemical transformation to solid products, chemical degradation to form biodegradable contaminants, physical elimination processes and incineration processes to form gaseous and solid residues that can be separated from the wastewater stream.

6.1. Precipitation

Precipitation involves the initiation of a chemical reaction to produce an insoluble component that can subsequently be separated by processes, such as sedimentation (see Section 5.2), air flotation (see Section 5.3), and/or filtration (see Section 5.4). Membrane filtration techniques (MF or UF) (see Section 5.5) may be utilised to protect downstream facilities or to prevent the discharge of hazardous particulates.

A precipitation facility usually involves an equalisation tank from which the wastewater is delivered to a stirred mixing tank. This is where the pH is adjusted and the chemical reagent is added. A further tank allows the addition of chemicals (e.g. alum, ferric chloride, proprietary polyelectrolytes) to aid flocculation and coagulation and to produce a denser sludge. The downstream components will, as a minimum, consist of a clarifier/sedimentation tank and relevant sludge collecting and dewatering systems. Precipitation is widely used as a source control technique for the removal of heavy metals. Chemical reagents such as calcium hydroxide (lime), sodium hydroxide (caustic soda), magnesium oxide and magnesium hydroxide can be used to precipitate arsenic, cadmium, trivalent chromium, copper, iron, lead, manganese, nickel and zinc. Hydroxide precipitation, particularly with lime, is the most common precipitation process because the chemical reagents are readily available, relatively inexpensive, easy to handle, and form sludges that dewater easily. Sulphide precipitation with reagents such as sodium sulphide, ferrous sulphide and polyorganosulphides can be used with cadmium, cobalt, copper, iron, mercury, manganese, nickel, silver, tin and zinc. Carbonate precipitation with reagents such as sodium carbonate (soda) and calcium carbonate (limestone) can be used with cadmium, lead, nickel and zinc. Because the metal sulphides are much less soluble than their hydroxide counterparts, sulphide precipitation can treat metals to lower emission concentrations. However, metal sulphides form very fine, hard to settle particles, which may eventually require membrane filtration, and generate large quantities of sludge (Kocuruk and Woodside, 1998).

In addition to its application for source control, precipitation can also used as a central treatment technique for the removal of phosphates, sulphates and fluorides through the addition of calcium salts (other than lime). With respect to phosphate, precipitation can

be used after the biological stage in a central WWTP, where the sludge is collected in the final clarifier. The factors influencing precipitation are pH, solubility product of the precipitant, ionic strength and temperature of the aqueous stream, and the presence of metal complexes. The optimum pH range for the precipitation of heavy metals, phosphate and fluoride is 9 to 12. When a wastewater contains a range of metals, it is difficult to optimise the precipitation process for each metal and this, together with the effect of the variable nature of the wastewater matrix, makes it difficult to report reliable performance efficiencies and achievable emission levels. When metals, such as copper and nickel are complexed or chelated they tend to be more soluble making the precipitation process more difficult. The nature of the collected sludge needs to be carefully assessed with regard to the most appropriate disposal route e.g. as a chemical waste.

6.2   Crystallisation

In contrast to precipitation, the removed solids are not formed by chemical reaction in the waste water, but are produced on seed material, such as sand or minerals, working in a fluidised-bed process – a pellet reactor system. The pellets grow and move towards the base of the cylindrical reactor. The driving force of the process is the reagent dosage and pH-adjustment. The velocity of the influent wastewater (40–120 m/h) entering at the bottom of the reactor keeps the pellets in a fluidised state (van der Molen, 1996). Providing that the process conditions at the bottom of the reactor are controlled to ensure that there is a high supersaturation of the desired salts, the fluidised bed provides a very large crystallisation surface allowing the majority of the anion or metal content to crystallise on the pellets in a fast and controlled reaction. Occasionally, some of the pellets are discharged and replaced by new seed material but there is no sludge production. The high purity of the recovered pellets facilitates the recycling and further use of metals.

In practice, a circulation system is operated in which the influent wastewater is mixed with circulated water containing lower anion or metal concentrations. This allows fluctuations in the influent flow and composition to be controlled and enables wastewaters with high contaminant concentrations (e.g. 10–100000 mg/l) to be treated through adjustment of the circulation ratio. The reagent dosage and the influent pH should be regularly monitored to maintain the optimum conditions for crystallisation. In practice, the best removal results are obtained when the reagents necessary to produce the crystallisation are added in excess of the required dose. If required, the effluent can be polished by sand filtration or membrane filtration located either inside the circulation loop or in the effluent outflow. The effluent can be used for the back-washing of conventional sand filters and the carry-over returned to the reactor after appropriate chemical additions.

Crystallisation is widely applied to the removal of heavy metals from wastewater streams and to their subsequent recovery. Anions such as fluoride, phosphate and sulphate can also be treated providing that they can be converted to insoluble or poorly soluble salts. An example of the use of crystallisation in the chemical industry is the recovery of zinc, nickel and tellurium from wastewaters (containing 50-250 mg metal/l)

produced during the production of rubber additives (van der Molen, 1996). Nickel and aluminium have been recovered from elastomer production wastewaters (containing 50 – 400 mg metal/l) with the crystallisation device working prior to a central biological WWTP. In principle, almost all heavy metals, metalloids and anions can be removed from all kinds of wastewater by crystallisation. The formation of salt pellets is enhanced when the solubility of the generated salt is low and the metal or anion crystallises quickly to form a stable crystal lattice. Metals are normally separated as carbonates, hydroxy carbonates, hydroxides, sulphides, phosphates, sulphates, or fluorides whereas anions are generally removed as calcium salts. A wide range of pollutant concentrations (10 mg/l–100 g/l) can be handled and removal capacities up to 100 kg metal/anion per hour per unit are achievable. Table 6.1 identifies the emission levels obtained for four metals (zinc, nickel, tellurium and aluminium) and the chemical feed conditions used in each case.

Table 6-1 The emission levels achievable for zinc, nickel, tellurium and alumimium following crystallisation in the presence of caustic soda and other chemicals.

Parameter	Emission level [mg/l]	Agent	Remarks
Zinc	1	soda, caustic soda	soda feed 50-250 mg/l, pH 10
Nickel	1	soda, caustic soda	soda feed 50-250 mg/l or 1000 mg/l, pH 10
Tellurium	1	manganese sulphate, caustic soda	pH 9, after filtration
Aluminium	20	sulphate, caustic soda	feed 50-400 mg/l

(van der Molen, 1996)

6.3 Chemical Oxidation

Chemical oxidation involves both the partial and complete degradation of many organic and inorganic compounds. With reference to pollutants, it is ideally the conversion to less harmful or hazardous compounds and/or to smaller and more easily biodegradable organic components. The oxidation process is often combined with other treatment systems (e.g. GAC adsorption, stripping, activated sludge biology) to obtain optimum results. The list of chemical oxidising agents which can be used includes chlorine, sodium or calcium hypochlorite, chlorine dioxide, ozone (with or without UV irradiation), hydrogen peroxide/UV irradiation, and hydrogen peroxide/ferrous salts (Fenton's agent). Oxidising agents do not discriminate and are capable of reacting with any oxidisable compounds within a wastewater. Hence, the presence of oxidisable compounds in addition to the target compound will increase the amount of oxidant required. Factors influencing the oxidation process include pH and the type and quantity of oxidisable material within the wastewater. The pH affects the oxidation rate by changing the free energy of the overall reaction, amending the reactivity of the reactants and affecting

specific OH⁻ or H_3O^+ ion catalysis. Metal salts, especially those of lead and silver, can also react with the oxidising agent and increase the required dosage or interfere with the treatment process.

Oxidation reactors are normally operated at pressures of up to 0.5 MPa (Bundesministerium für Umwelt, 2000) although hydrogen peroxide oxidation proceeds at atmospheric pressure and room temperature and is normally complete within 60–90 minutes (Ullmann's Encyclopedia of Industrial Chemistry, 2000). When UV irradiation is required as an accelerator, the reactor has to be constructed using quartz and the radiation source (e.g. a low-pressure mercury lamp) can be positioned either outside the quartz tubes with the wastewater on the inside or vice versa. If ozone is involved in the process, it has to be generated *in situ* as it is an unstable compound. Any surplus ozone has to be eliminated according to strict safety requirements. With hydrogen peroxide as the oxidation agent, a granular activated carbon (GAC) adsorber is normally used to eliminate surplus agent. The use of chlorine requires the use of special equipment, such as titanium manufactured vessels with additional installations (e.g. sulphite) to eliminate surplus chlorine.

Chemical oxidation is normally applied when the wastewater contains contaminants that are either not readily biodegradable or not biodegradable at all (e.g. inorganic compounds). Refractory COD concentrations over a wide range from >1 g/l down to less than 1 µg/l can be treated successfully (Naval Facilities Engineering Service Center (USA), 1998). Chemical oxidation is also appropriate where the contaminants might disturb the biological or physico-chemical processes in a downstream WWTP or have properties which make them too harmful to be released directly into a sewer system. Examples of such contaminants are oil and grease, phenols, polycyclic aromatic hydrocarbons (PAHs), organic halides, dyes (with Fenton's agent), pesticides, cyanides, sulphides, sulphites and heavy metal complexes. Partially biodegradable contaminants may be treatable with specially adapted micro-organisms but in the absence of a central biological WWTP, chemical oxidation is often the recommended treatment option.

Oxidation with chlorine or sodium chlorite can be used under special conditions to remove organic contaminants, even halogenated derivatives. An example is the SOLOX®-Process to eliminate (at elevated pressure and temperature) COD/TOC and AOX from wastewater originating from epichlorohydrin production. However, the use of chlorine, hypochlorite and chlorite (or the respective halogen compounds) can result in the formation of toxic halogenated compounds such as the trihalomethanes, bromodichloromethane, dibromochloromethane and chloroform. Wastewater treated by chlorine oxidation has to have surplus chlorine or hypochlorite removed before it is discharged from the treatment site. Chlorine dioxide does not produce these troublesome by-products and also yields more biodegradable intermediate products.

A primary advantage of ozone oxidation is the avoidance of chlorinated by-products. Ozone can completely oxidise low aqueous concentrations of organics and can partially degrade refractory compounds. Compounds that can be treated with ozone include alkanes, alcohols, ketones, aldehydes, phenols, benzene and its derivatives, and cyanide and this list can be expanded to include chlorinated organic compounds and

pesticides when ozonation is accompanied by UV irradiation. As ozone is only slightly soluble in water, factors that affect the mass transfer between gas and liquid phases are important and include temperature, pressure, contact time, contact surface area (bubble size), and pH. Hydrogen peroxide is typically used as an oxidising agent in conjunction with UV light, ozone and/or metal catalysts (e.g. Fenton's reagent which is hydrogen peroxide with iron as a catalyst). Hydrogen peroxide/UV light has been shown to be effective in oxidising benzene, chlorobenzene, chloroform, chlorophenol, 1,1-dichloroethane, dichloroethene, phenol, tetrachloroethylene, 1,1,1-trichloroethane, trichloroethylene, toluene, xylenes and many other organic compounds.

For oxidation using hydrogen peroxide, the COD elimination of various organic substances as a function of oxidising agent utilisation is illustrated in Table 6.2. Use of chlorine/hypochlorite as the oxidising agent in the SOLOX®-Process can reduce TOC by >90% at a feed concentration of 1 g/l and AOX by 80% at a feed of 40 mg/l.

Table 6-2 COD elimination of various substances as a function of H_2O_2 utilisation

Substance	Dosage H_2O_2 / COD [%]	COD elimination [%]
Morpholine	100	20
2-Aminoethanol	100	37
Diethyleneglycol	100	45
Polyethyleneglycol	100	35
Hexamethylenetetramine	100	32
2,4-Difluoro-5-chloro-6-methylpyrimidine	100	30
Phenyltrifluoroethylcarbamide	80	75
Ammonium trifluorothyldithiocarbamate	80	79

(Ullmann's Encyclopedia of Industrial Chemistry, 2000)

6.4   Wet Air Oxidation

Wet air oxidation is the oxidation of soluble or suspended components in wastewaters using the oxygen present in air as the oxidizing agent. The oxidation reactions occur in superheated water at temperatures of 150ºC to 320ºC i.e. above the normal boiling point of water but below the critical point (374°C). The system must be maintained under pressure (e.g. >2 Mpa) to avoid excessive evaporation of water and because a liquid phase is necessary to support most oxidation reactions. Many compounds oxidize under wet oxidation conditions that would not oxidize under dry conditions at the same temperature and pressure. Organic compounds are converted into carbon dioxide, water and biodegradable short chain acids and inorganic contaminants such as sulphides and cyanides can also be oxidised. The wet oxidation process can pre-treat difficult wastewater streams, making them amenable for discharge to a conventional biological treatment plant for polishing. Wastewaters treated by wet air oxidation are generally those with dissolved or suspended contaminant concentrations between 500 and 50,000 mg/l. Below 500 mg/l, oxidation rates are too slow and above 50,000 mg/l, incineration may be more feasible.

Commercial systems (see Figure 6.1) typically use a bubble column reactor (made from special titanium alloys), where air is bubbled through a vertical column that is full of the

hot and pressurized wastewater. Fresh wastewater enters the bottom of the column and oxidized wastewater exits the top. The heat released during the oxidation is used to maintain the operating temperature. Variations on the high pressure/high temperature system include a low pressure version and also one that includes the use of catalysts. Catalysts enable operating temperatures to be lowered but the catalyst needs to be removed from the effluent to avoid contamination and to minimise operating costs.
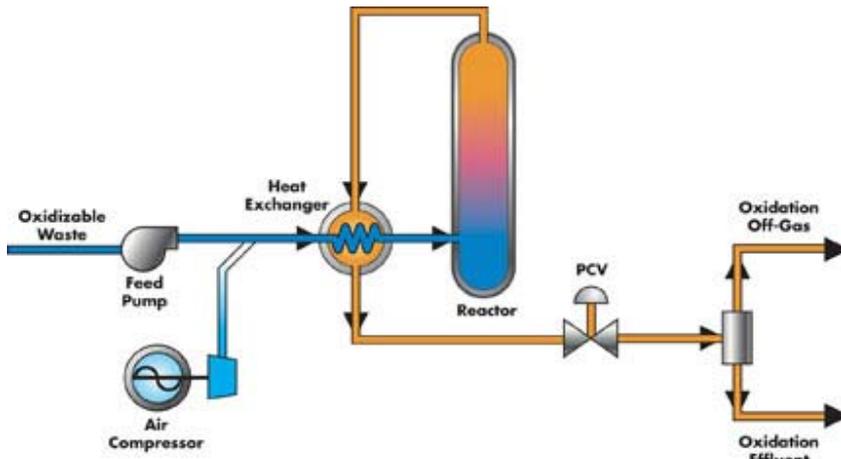
Figure 6-1 Diagrammatic representation of a wet air oxidation system (Zimpro® Wet Air Oxidation)

Wet air oxidation is used for wastewaters containing contaminants that are either not readily biodegradable, that might disturb the biological process in a downstream biological WWTP, or that have properties too harmful to allow them to be released into an ordinary sewer system. The technique is also used for sludge treatment. Specific examples of its use include the oxidation of phenol and naphthalene derivatives at 120–150ºC and the breakdown of chlorinated aromatics in a catalysed process at 120–190ºC. Sulphite from dye manufacturing is converted to sulphate in a two-step, homogeneously catalysed process at 120-140 ºC and 0.6 MPa (Ullmann's Encyclopedia of Industrial Chemistry, 2000).

COD reductions of 60-90% (Bundesministerium für Umwelt, 2000) have been reported for wet air oxidation. More specifically, an 85% removal of COD by wet oxidation (190°C, 2 MPa) followed by 90% reduction after a subsequent biological clarification step, bringing the overall COD removal to 98% has been reported (Ullmann's Encyclopedia of Industrial Chemistry, 2000). In comparison, the high pressure process (250°C, 7 MPa) has the ability to remove 99% of COD at an initial concentration of 30 g/l (Winter, 2000). When applied to a range of substituted aromatics, removal rates consistently above 75% and as high as 99% have been achieved (Ullmann's Encyclopedia of Industrial Chemistry, 2000). The performances of wet air oxidation when applied to pesticides are shown in Table 6.3.

Table 6-3 Pesticide removal efficiencies using wet air oxidation as an industrial treatment process

Contaminant	Influent concentration [μg/l]	Effluent concentration [μg/l]
Aldrin	500	<50 (>90%)
DDT	21000	<300 (>98.5%)
Endosulfan	18400	291 (98.5%)
Endrin	3600	<100 (>97%)
2,4-Dichlorophenol	180	<3.1 (>98%)

(Environment Agency (UK), 1997)

In addition to further treatment being provided for the oxidised effluent, the off-gases (e.g. carbon monoxide and lower hydrocarbons) require downstream treatment through processes such as adsorption, gas scrubbing and/or thermal/catalytic oxidation of the waste gas. In certain circumstances it is possible for dioxins to be produced during the oxidation process necessitating their removal before the discharge of either gaseous or aqueous effluents.

6.5   Supercritical water oxidation

Supercritical water oxidation (SCWO) is similar to wet air oxidation in that a combination of high temperatures and pressures are used to oxidise organics. However, these are considerably elevated to pressures above 22 MPa and temperatures higher than 374 °C. The conditions applied are above the thermodynamic critical point so that the water becomes a fluid with unique properties that can be used to advantage in the destruction of hazardous wastes such as PCBs. The fluid has a density between that of water vapour and liquid at standard conditions, and exhibits high gas-like diffusion rates along with high liquid-like collision rates. In addition, solubility behaviour is reversed so that organics (e.g. chlorinated hydrocarbons) become soluble in water, allowing efficient oxidation in the presence of a dissolved oxidising agent. Reaction times are very short (a few seconds to less than a minute) and treatment efficiencies typically approach 100%. This technique has the capability of treating many different kinds of organics including polyaromatic hydrocarbons, chlorinated hydrocarbons, PCBs, paint, oil, dyes, and pulp and paper wastes (Jensen, 1994). The reversed solubility also causes salts to precipitate out of solution, meaning they can be treated using conventional methods for solid-waste residuals. SCWO can be classified as green chemistry or as a Clean Technology.

The components of an SCWO process are shown in Figure 6.2. The wastewater is brought to the supercritical pressure by a high-pressure pump before it enters the economiser, where the feed is preheated by the reactor effluent. At start-up, or if the organic concentration in the waste water is less than 4 %, the feed has to be heated further to reach the supercritical temperature range. When oxygen is added to the feed the temperature in the reactor will rise to about 600°C. The reactor effluent flows into the economiser, then through a heat recovery steam generator and through an effluent

cooler. Finally a control valve drops the effluent pressure to atmospheric conditions and the liquid and gas phases are separated. Reaction vessels for SCWO must be highly corrosion resistant because of the aggressive nature of supercritical water and the oxidation products, such as a variety of acids. The organic carbon content of wastewater is converted to carbon dioxide, organic and inorganic nitrogen compounds are converted into nitrogen, organic and inorganic sulphur compounds are converted to sulphuric acid, and organic and inorganic halogen compounds are converted to the corresponding acid.

SCWO is applied to contaminants with low biodegradability and/or high toxicity in the effluents generated by the chemical, petrochemical and pharmaceutical industries. It destroys dioxins and PCBs and because of the relatively low temperature range of 400–600 °C there is limited production of NO_x. However the gaseous effluent can contain traces of nitrous oxide and acetic acid, as well as hydrogen halides and sulphuric acid vapours, which need to be treated in downstream waste gas facilities. Inorganic salts can be a problem because they are sparingly soluble under the applied conditions and thus may precipitate on the reactor walls and components.
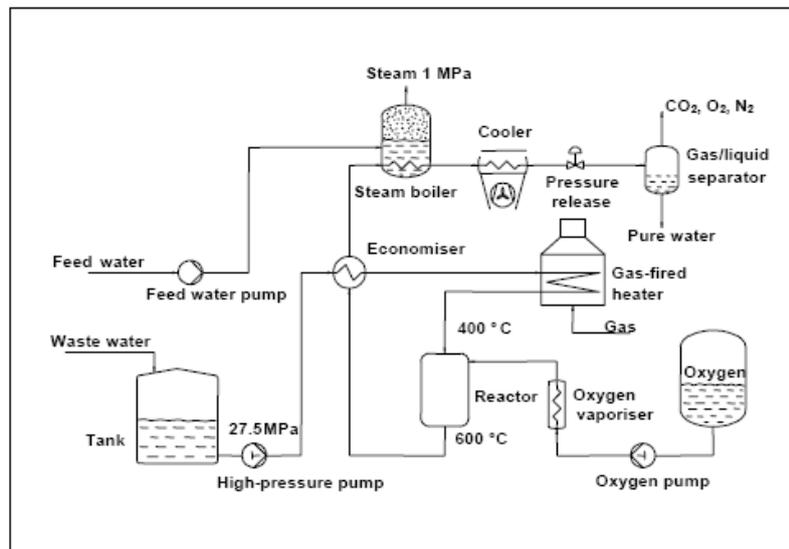
Figure 6-2 A simplified flow diagram of the supercritical water oxidation process.

The excellent removal performances for organic pollutants are shown in Table 6.4 together with the operating temperatures and times for the SCWO process.

Table 6-4 SCWO performance levels for a range of organic compounds

Parameter	Performance rate [%]	Remarks
Organic compounds	>99	
1,2,4-Trichlorobenzene	99.99	495 °C, 3.6 minutes
4,4- Dichlorobiphenyl	>99.99	500 °C, 4.4 minutes
DDT	>99.99	505 °C, 3.7 minutes
PCB 1234	99.99	510 °C, 3.7 minutes
PCB 1254	99.99	510 °C, 3.7 minutes
Dioxin	>99.99	574 °C, 3.7 minutes

(Environment Agency (UK), 1997)

6.6   Chemical Reduction

Chemical reducing agents, such as sulphur dioxide, sodium hydrogen sulphite, ferrous sulphate and sodium sulphide are able to reduce inorganic pollutants and, to a lesser extent, organic pollutants producing less toxic compounds. This process is applied to wastewaters containing contaminants that are not readily removable or have properties too harmful to allow them to be released into a common sewer system. A commonly used example is the reduction of chromium(VI), as chromate or dichromate, to chromium(III) using sulphur dioxide. The reduction reaction is highly dependent on both pH and temperature. A pH range of between 2 and 3 is normal if complete reduction is required and at pH >5 the reduction rate is to slow. Other frequently used examples of chemical reduction are chlorine or hypochlorite to chloride and hydrogen peroxide to water and oxygen. Chemical precipitation is commonly employed as a downstream operation in connection with chemical reduction.

The basic facility for chemical reduction is a continuously stirred tank reactor (CSTR), tailor-made according to process requirements, e.g. corrosion- and pressure-resistant material and appropriate ducting for any noxious gases produced. The conversion of chromium (VI) to chromium (III) typically requires a retention time of around 45 minutes for complete mixing and reduction to occur. The reaction tank has an electronic controller – recording device to control process conditions with respect to pH and oxidation-reduction potential (ORP). If the reducing agent is gaseous sulphur dioxide, this is metered into the tank to maintain the ORP in the range between 250 and 300 mV. Monitoring of the ORP enables the process to be operated automatically. Sulphuric acid is introduced to maintain the pH between 1.8 and 2.0. Wastewaters containing a wide range of pollutant concentrations (from >1 g/l to <1 mg/l) can be treated by chemical reduction.

6.7.   Chemical hydrolysis

Hydrolysis is a chemical reaction in which organic and inorganic constituents react with water and break into smaller (and less toxic) compounds. It is a destructive technology in which the original molecule forms two or more new molecules. In some cases, the reaction continues and other products, usually short-chained and easily biodegradable compounds, are formed. Hence, additional downstream treatment is generally required such as that provided by a central biological WWTP. Other downstream treatment operation options include GAC adsorption and air/vapour stripping. Because some pesticide active ingredients are susceptible to hydrolysis, this can be an effective initial treatment technology for these substances in wastewaters.

The primary design parameter considered for hydrolysis is the half-life, which is the time required to react 50% of the original compound. The half-life of a reaction generally depends on the reaction pH and temperature and the nature of the reactant molecule. Hydrolysis reactions can be catalyzed at low pH (e.g. by addition of sulphuric acid), high pH (e.g. by addition of sodium hydroxide), or both depending on the reactant molecule. In general, increasing the temperature increases the rate of hydrolysis. Identifying the best conditions for the hydrolysis reaction results in a shorter half-life, thereby reducing both the size of the reaction vessel and the treatment time required.

Hydrolysis reactors normally operate at ambient pressure and temperature. If high temperatures are required, the reactor will be fitted with a heat exchanger system with pre-heating facilities for the wastewater input. Autoclaves may be required for temperatures well above 100 °C and pressures up to 0.5–1 MPa. Processes are batch-based and therefore require operators to charge and empty the reactor vessel. Because of the strongly acidic or basic conditions employed, special corrosion-resistant equipment needs to be used and any surplus reagent has to be neutralised after the treatment operation. Chemical neutralisation will result in the production of an additional salt load which if discharge to receiving waters is not feasible represents a sludge in need of disposal.

Chemical hydrolysis is applied to wastewater streams containing contaminants that are not readily biodegradable, that might disturb the biological process in a downstream biological WWTP and/or have properties too harmful to allow them to be released into the sewer system. Examples of contaminants to which the hydrolysis process has been applied include organic halides, pesticides, organic cyanides, organic sulphides, organophosphates, carbamates, esters and amides. Treatable concentration ranges are between 1 mg/l and 100 g/l although this will be dependent on the water solubility of the starting material. Removal efficiencies are strongly dependent on the chemical structure of the compound undergoing hydrolysis, pH and temperature. Quantitative degradation can be achieved, but pilot studies are advisable to determine the optimum treatment conditions.

6.8   Nanofiltration and Reverse Osmosis

Nanofiltration (NF) and reverse osmosis (RO) are membrane processes which involve the permeation of a liquid through an appropriate membrane under pressure, resulting in separation into a clean stream (which passes through the membrane) and the concentrate (containing retained particles, ions and/or organic molecules). In nanofiltration the separation is determined by the pore size of the membrane which is less than that used in other membrane filtration techniques (microfiltration and ultrafiltration; see Section 5.5). Reverse osmosis involves forcing the solvent from a region of high solute concentration through a semipermeable membrane to a region of low solute concentration by applying a pressure in excess of the osmotic pressure. Hence it is the reverse of normal osmosis in which a solvent naturally moves from an area of low solute concentration, through a membrane, to an area of high solute concentration when no external pressure is applied. The successful application of reverse osmosis requires the exertion of a pressure on the high concentration side of the membrane, which exceeds the natural osmotic pressure of the wastewater being treated relative to clean water. The feed to the membrane needs to be particle-free to prevent rapid contamination of the membrane and an associated reduction in its effectiveness. The typical characteristics of NF and RO membranes are listed in Table 6.5.

Table 6-5 Physical characteristics associated with Nanofiltration (NF) and Reverse Osmosis (RO)

Parameter	Nanofiltration	Reverse osmosis
Pore diameter [μm]	0.01–0.001	<0.001
Operating pressure [MPa]	0.5-3	2-100
Cut-off size [nm]	>1 200–1000 g/mol	<1000 g/mol
Permeate flow [l m^{-2} h^{-1}]	<100	10–35
Cross flow speed [m/s]	1-2	<2
Membrane type	Polymeric asymmetric or composite	polymeric asymmetric or composite
Membrane configuration	spiral-wound tubular	spiral-wound tubular

(Environment Agency (UK), 1997; Ullmann's Encyclopedia of Industrial Chemistry, 2000; ATV Handbuch Industrieabwasser, 1999)

NF membrane materials are typically cellulose acetate or polyamide based with the latter possessing a superior performance for the removal of organic molecules. Membrane materials for RO are organic polymers, such as cellulose acetate, polyamide, polyimide, polycarbonate, polyvinylchloride, polysulphone, polyethersulphone, polyacetal, copolymers of acrylonitrile and vinyl chloride, polyelectrolyte complexes, cross-linked polyvinyl alcohol and polyacrylates. These membrane materials have relatively low thermal and chemical resistance which limits their application to a restricted pH and temperature range (18-30°C). For both techniques, cross-flow operation is employed so that the permeate flow is directed perpendicular to the feed flow and the impurities remain in the feed which leaves the membrane system as a

concentrated waste stream. The objective, subject to energy consumption limitations, is to maintain a minimum velocity as close as possible to 2 m/s across the membrane surface.

In practice, the optimum modification for a particular application will depend on the nature and composition of the wastewater. Normally, there will be a pre-treatment step employing chemical clarification (precipitation, coagulation/flocculation or flotation) and subsequent filtration, or using filtration and subsequent UF. However, even under the best pre-treatment regimes and programmes, membranes are susceptible to fouling and will deteriorate in performance if cleaning is not ensured. Cleaning agents include acids, alkalis, oxidising agents, detergents and organic solvents. Ideally, membrane systems should be designed in such a way that they can be taken offline and cleaned mechanically or chemically. They can be arranged as modules which are either in parallel (to provide the necessary hydraulic capacity) or in series (to increase the degree of efficiency).

NF and RO have different applications because of the different properties they exhibit in the migration of molecular particles through the membrane surface. NF is mainly used to remove larger organic molecules and multivalent ions in order to recycle and re-use the wastewater or to reduce its volume and simultaneously increase the concentration of contaminants to such an extent that subsequent destruction processes are feasible. RO is utilised as a process to separate water and the dissolved constituents down to the size of ionic species and is capable of producing a treated water with a high grade of purity. Hence the widescale use to provide drinking water through desalination. With respect to wastewaters, it has been used for the final removal of degradable components (in the absence of biological treatment), heavy metals and toxic components. The concentrated waste streams may be further processed where this is economically viable.

Very good separation efficiencies are attainable using these techniques but high pressures are required and the permeate fluxes tend to be low (see Table 6.5). The removal performance efficiencies for a range of inorganic and organic pollutants are listed in Table 6.6.

Membrane treatment produces a waste stream (concentrate) of approximately 10 % of the original feed volume, in which the target substances are present at levels approximately 10 times their concentration in the waste water. An assessment needs to be made as to whether this residue can be recycled, disposed of or whether further treatment is necessary. For organic substances the concentration increase might improve the conditions for subsequent oxidative destruction processes.

Table 6-6 Examples of removal efficiencies achievable by nanofiltration and reverse osmosis

Parameter	Removal efficiency (%)	
	NF	RO
Inorganic mercury	>90	
Organic mercury	>90	
Cadmium compounds	>90	
Tetrachloromethane	96	
1,2-dichloroethane	71	
Trichlorobenzene	96	
Perchloroethene	90–92	
Atrazine	>70	84–97
γ-Hexachlorocyclohexane		99
DDT		100
Aldrin		100
Dieldrin		100
Dichlorvos		98
Simazine		95
Trifluralin		99
Fenitrothion		99
Azinphos-methyl		98
Malathion		99
TOC	80-90	

(Environment Agency (UK), 1997)

6.9   Adsorption

Adsorption is a well established and widely used technique for the removal of soluble substances (solutes) from the wastewater phase to the surface of solid, highly porous, particles (the adsorbent). Each adsorbent has a finite capacity for a particular compound which is being removed. When this capacity is exceeded, the adsorbent is 'spent' and has to be replaced by fresh material. The spent adsorbent can either be regenerated or incinerated.   A list of commonly used adsorbents in wastewater treatment and their properties is provided in Table 6.7 (Ullmann's Encyclopedia of Industrial Chemistry, 2000). Zeolites can also be used as efficient adsorbers.

Different contact processes are possible for carrying out adsorption including mechanical mixing in a batch treatment. Continuous treatment can be achieved by allowing the wastewater to percolate through a fixed-bed packed column. Usually, at least two columns are employed and operated alternatively for adsorption and backwashing. An alternative approach involves continuous percolation through a pulse-bed or moving-bed in which wastewater and adsorbent are fed in a counter-current manner through the column. Ideally the wastewater needs to be as free from suspended solids as possible (using upstream filtration) to limit the liability to clogging and blockage within the column. The maximum TSS limit for fixed bed adsorbers is 20 mg/l and for moving bed adsorbers 10 mg/l. An example of an adsorber vessel is shown in Figure 6.3. These are usually built of corrosion-resistant material, e.g. lined carbon-steel, stainless steel or fibreglass-reinforced plastic (FRP).

Table 6-7 Physicochemical characteristics of adsorbent materials used in industrial wastewater treatment.

Adsorbent	Form	Specific surface area [m^2/g]	Pore volume [cm^3/g]	Bulk density [g/l]
Activated carbon	granular	500-1000	0.3 -0.8	300-550
	powder	600-1500	0.3-1.0	
Lignite coke	granular, powder	200–250	<0.1	about 500
γ-Aluminium oxide	granular, powder	300–350	0.4–0.5	700–800
Adsorber resins	granules	400-1500	porosity 35–65 v-%	650-700

The adsorbent most commonly used in the chemical sector is activated carbon, either in granular form (GAC) in columns or as a powder (PAC) dosed to a treatment tank. GAC adsorption has the ability to remove soluble organics and inorganic compounds such as sulphides and heavy metals from industrial wastewaters. It has been particularly widely used as a tertiary process to adsorb the relatively small quantities of organic pollutants remaining in wastewaters following biological or physical-chemical treatment. The ranges of chemicals amenable to adsorption by GAC are identified in Table 6.8. The contaminants are physically attracted or adsorbed on the surface of the carbon. Adsorption capacities are high because of the porous nature of GAC provides a large surface area relative to its volume. GAC is normally regenerated by thermal reactivation at temperatures of about 900-1000 °C. This regeneration process releases off-gases that contain the thermal and chemical decomposition products of the adsorbed compounds. For each regeneration stage, a proportion of about 10 % of the adsorbent is lost (Environment Agency (UK), 1997) and has to be replaced by fresh GAC. As regeneration is relatively expensive, plants are usually designed to give a period of at least six months between regeneration cycles.

Table 6-8 Types of organic compounds which can be removed by GAC adsorption

Category of organic compound	Examples
Aromatic solvents	Benzene, toluene, xylene
Polynuclear aromatics	Naphthalene, biphenyl
Chlorinated aromatics	Chlorobenzene, PCBs, endrin, toxaphene, DDT
Phenolics	Phenol, cresol, resorcinol, nitrophenols, chlorophenols, alkyl phenols
Aromatic amines & high molecular weight aliphatic amines	Aniline, toluene diamine
Surfactants	Alkyl benzene sulfonates
Soluble organic dyes	Methylene blue, textiles, dyes
Fuels	Gasoline, kerosene, oil
Chlorinated solvents	Carbon tetrachloride, percholoroethylene
Aliphatic & aromatic acids	Tar acids, benzoic acids
Pesticides/herbicides	2,4-D, atrazine, simazine, aldicarb, alachlor, carbofuran

(US EPA, 2000)
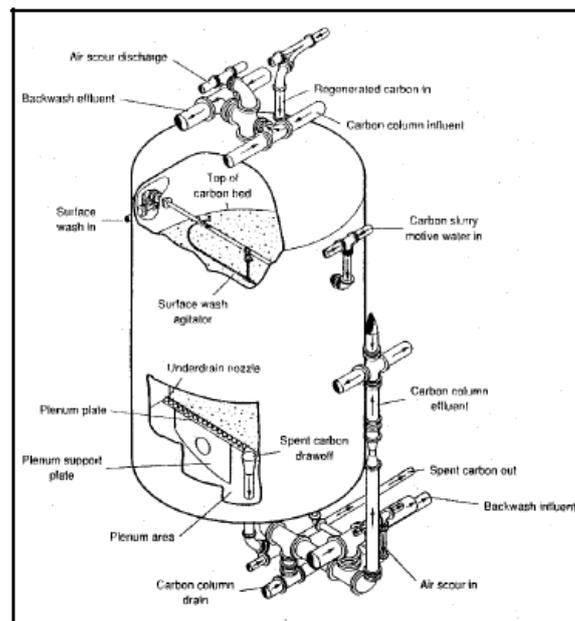
Figure 6-3 A conventional down flow activated carbon adsorber (Metcalfe and Eddy Inc, 1991)

Adsorption by PAC can be applied to the same contaminants as GAC. It is added to the wastewater to be treated as a slurry and subsequently removed by separation processes such as sedimentation and filtration. PAC can also be added to the wastewater stream at the same point as inorganic coagulants and removed by existing sedimentation and filtration devices. In this role it can be used as an intermittent adsorber of organics by dosing as and when it is needed. It is also used in emergencies to remove refractory, hazardous or toxic substances that may have escaped into a

sedimentation tank, activated sludge tank or other vessel. Normally PAC is not regenerated but becomes part of the sludge to be disposed of.

The characteristics of other adsorbents used in the treatment of wastewaters are discussed below:
- Lignite coke can be used as a direct replacement for GAC and although cheaper it has a lower adsorption efficiency.
- Activated aluminium oxide is used to adsorb hydrophilic substances, e.g. fluoride and phosphate. When contaminated with inorganic substances, it is regenerated chemically whereas organic contaminants can be removed thermally at 750 °C.
- Adsorber resins are based on synthetic organic polymer materials and find special uses where compound selectivity is important, low effluent concentrations are required, carbon regeneration is impractical, or the waste to be treated contains high levels of inorganic dissolved solids. They are regenerated chemically with solvents such as methanol or acetone.
- Zeolites are utilised to remove ammonia or heavy metals, e.g. cadmium. They are regenerated by elution with solutions of sodium chloride mixed with caustic soda or lime.

The maximum acceptable pollutant concentrations are 100 g/l in the absence of adsorbent recovery and 500 g/l when adsorbent recovery is in place. Several characteristics of the contaminant are known to influence the removal process. Carbon adsorption is most effective at removing organic compounds that have low polarities, high molecular weights, low water solubilities and high boiling points. The impact of polarity can be shown by comparing the removal efficiencies of benzene (95%) and methanol (4%) with a GAC column at feed concentrations of (1000 mg/l). Branched chain organic compounds are more sorbable than straight chain compounds (Nalco Chemical Company, 1988). A high content of macromolecular compounds decreases efficiency and may cause irreversible blockage of active sites.

The efficiency of adsorption processes varies widely according to the wastewater composition and feed concentration. Therefore it is preferable if influent concentrations can be quoted in conjunction with removal performances. An extensive list of examples is shown in Table 6.9.

6.10   Ion Exchange

The ion exchange process describes the purification, separation, and decontamination of aqueous and other ion-containing solutions using solid polymer or mineral based 'ion exchangers'. Typical ion exchangers are ion exchange resins (functionalized porous or gel polymers), zeolites, montmorillonite, clay, and soil humus. They are either cation exchangers that exchange positively charged ions or anion exchangers that exchange negatively charged ions. There are also amphoteric exchangers that are able to exchange both cations and anions simultaneously. Ion exchangers can possess binding preferences for certain ions or classes of ions, depending on their chemical structure. This can be dependent on the size of the ions, their charge, or their structure.

The feed to ion exchange resins should contain <50 mg/l of suspended particles to prevent plugging and therefore gravity or membrane filtration are appropriate pre-treatments. A typical ion exchange operation cycle consists initially of passing the contaminated solution through a packed resin column contained in vertical cylindrical pressure vessel with corrosion-resistant linings. An even distribution of the influent wastewater is ensured by an appropriately designed inlet distribution system to prevent hollowing out of flow channels within the resin bed. This is followed by a backwash stage in which any accumulated particles are removed and the ion exchange resin bed is reclassified. A critical stage is the regeneration process in which the ion exchange resin is reloaded with the original ions (using a low volume of high concentration solution) and the unwanted ion species are released to the regeneration solution. A slow rinse or displacement process uses a slow water-flow through the bed to displace the regeneration solution and is followed by a fast rinse to remove the remaining traces of the regeneration solution, including any residual hardness.

Table 6-9 Removal efficiencies for a range of pollutants by different adsorbents.

Parameter	Performance Rate [%]						Remarks
	GAC	PAC	Lignite	Al$_2$O$_3$	Resin	Zeolite	
Inorganic Hg	80						feed 29 µg/l
Organic Hg	80						low feed
γ-Hexa-chloro-cyclohexane	93						feed 7.7 µg/l
		99					feed 10 µg/l PAC 85 mg/l
DDT	97-99.9						
Aldrin	88-93						
		90-99					PAC 5-20 mg/l
Dieldrin	86-98						
		99 [0.1 µg/l]					feed 10 µg/l, PAC 126 mg/l
Atrazin	84						feed 0.61 µg/l
Endrin		<0.1 µg/l					feed 10 µg/l, PAC 70 mg/l
Dichlorvos		99					
TCB		70-93					feed 200 µg/l PAC 20 mg/l
Fenitrothion		99					
Azinphosmethyl		99					
Ammonia						98 [0.5 mg/l]	feed 25 mg/l
COD	50						moving bed, feed 5 g/l
	67-75 [<100 mg/l]						feed concentration 300-400 mg/l
Phenols	75						moving bed, feed 70 mg/l
	60-80 [1-2 mg/l]						feed concentration 5 mg/l
AOX	>90						moving bed, feed 60 mg/l

(Environment Agency (UK), 1997; Bundesministerium für Umwelt, 2000; North Ostrobothnia Regional Environment Centre, 2000)

Ion exchange is feasible as an end-of-pipe treatment, but its greatest value lies in its recovery potential e.g. for rinse water and process chemicals. Typical influent concentrations of ionic and ionisable species in wastewater are between 10 and 1000 mg/l. Heavy metals as either cations (e.g. Cr^{3+} or cadmium and its compounds) or anions (e.g. chromate, CrO_4^-) are effectively removed as are ionisable inorganic compounds. Organic compounds which can exist in the soluble ionic state can be removed by ion exchange. Compounds in this category include carboxylic acids, sulphonic acids, some phenols, amines as acid salts, quaternary amines, alkylsulphates and organic mercury.

Using the ion exchange technique, typical effluent ion concentrations that can be achieved are in the range of 0.1–10 mg/l from influent concentrations of 10–1000 mg/l. This corresponds to removal rates of 80–99 % and has been observed for copper, nickel, cobalt, zinc, chromium(III), chromium(VI), iron, sulphate and nitrate (VITO, 2000). The regeneration of ion exchange resins results in a small volume of concentrated acid or salt solution (containing the removed ions originating from the resin) and this enriched liquid has to be treated separately to remove these ions, e.g. heavy metals by precipitation.

6.11   Solvent Extraction

Solvent extraction is a technique used to separate compounds based on their relative solubilities in two different immiscible liquids, usually water and an organic solvent. When applied to the wastewater phase, it involves the transfer of water soluble contaminants into a solvent which possesses a greater dissolution capacity for the contaminant and is easily separated from the wastewater because of large density differences. The selected solvent should also have low toxicity, be thermally stable and be easily evaporated under conditions of applied distillation. Examples of solvents which might be used include light crude oil, toluene, pentane and hexane.

Column extraction is the normal operating mode and can have multiple stages with the wastewater and the organic solvent being brought into contact through either concurrent or countercurrent interaction. Different methodologies can be employed to achieve the best contact between the two liquid phases e.g. counter-current cascades, packed columns, spray towers etc. Following separation, the organic extract can be directed to a distillation or steam stripping unit to isolate the dissolved organics from the solvent and the solvent can be recycled back to the extraction process. However, solvent regeneration can be complex and expensive. The extracted contaminants have to be disposed of as chemical waste, normally by incineration. The remaining waste water phase, known as the raffinate, usually requires removal of any dissolved solvent e.g. by stripping or GAC adsorption.

Wastewaters to be treated by solvent extraction should preferably be almost free of suspended solids and/or emulsions. Solvent extraction is applicable to a variety of organic contaminants (including refractory and/or toxic compounds) and some metal complexes, when a suitable solvent exists and if the contaminant concentration is not too low. Under these circumstances it is often used as a pre-treatment prior to

adsorption and/or biological treatment. Some examples of the use of solvent extraction are:

- removal of phenol (phenosolvan process)
- recycling of metals, such as zinc
- recycling of substances from mother liquors
- removal of phosphoric acid esters
- removal of chloro-aromatics
- pretreatment concentration of aromatic sulphonic acids (Bundesministerium für Umwelt, 2000)

Important factors influencing solvent extraction are the relative solubilities of the organic components in the solvent, selectivity value (the ratio of the equilibrium concentrations of the contaminant in the solvent and the wastewater), temperature, pH, mixing conditions, and settling time for separation. Temperature and pH affect equilibrium conditions. Sufficient time needs to be allowed for settling to separate the extract and the raffinate. When the optimum conditions are achieved high removal efficiencies are possible e.g. phenol can be removed from a feed solution containing 10 g/l at a 99% performance rate.

6.12   Distillation/Rectification

Distillation or rectification is the separation of volatile components from wastewater by using differences in vapour pressures (or boiling points) between contaminants and water to transfer the former into the vapour phase. Azeotropic mixtures require appropriate additives to make distillation feasible. The enriched vapour phase is subsequently condensed and collected. There are two general types of distillation, batch distillation or continuous fractional distillation. Batch distillation is typically used for small amounts of solvent wastes that are concentrated and consist of very volatile components that are easily separated from the non-volatile fraction. If a wastewater contains a mixture of volatile components that have similar vapour pressures, separation is more difficult and continuous fractional distillation is required. This process is performed in columns, equipped with plates or packing material, and a downstream condenser device. The heating is usually done by direct steam injection to avoid local overheating. Operating the process under vacuum conditions lowers the boiling temperature and allows the separation of less volatile substances.

Wastewater distillation has limited applications because of high energy consumption and the feed concentration needs to be sufficiently high for distillation to become economically feasible. Examples include the recovery of solvent after wastewater extraction, recovery of solvent from wastewater, e.g. separation of alcohols from methyl cellulose production, treatment oil emulsions, and pre-treatment to remove the main contaminant content from the wastewater stream (to recover it) and afterwards subject the wastewater to further downstream treatment.   Details of the performance capabilities of the distillation technique are provided in Table 6.10 for a range of organic contaminants.

Table 6-10 Performance data for the removal of a range of organic contaminants from wastewaters by distillation.

Parameter	Performance rate [%]	Emission level [mg/l]	Remarks
Phenols	96	2000	feed 50 g/l
Methanol	97.5	2000	feed 80 g/l
Epichlorohydrin (ECH)	90	700	feed 7 g/l
Aniline	97.5	100	feed 4 g/l
Chlorobenzene	90	10	feed 100 mg/l

(Bundesministerium für Umwelt, 2000)

6.13   Evaporation

Evaporation of wastewater is effectively a distillation process in which the volatile substance is water so that when removed a lower volume of a more concentrated solution or a residue is left behind. This technique is therefore used when concentrated wastewater streams are required or recommended. The volatilised steam is collected in a condenser and the condensed water may be recycled. However, volatile contaminants may pollute the condensate involving subsequent treatment. The process can be enhanced by applying vacuum conditions which lower the boiling temperature and also enable the recycling of substances which would otherwise decompose. Typical operating conditions are 12–20 kPa and 50–60°C and hence there is a relatively high energy consumption. Thin film evaporators, dryers and aqueous evaporators are examples of evaporation equipment used for treating wastewaters. They are usually operated in series, with the condensation heat of one stage being used to heat the condensate (i.e. wastewater) of the preceding stage.

Evaporation can be used to recover or remove crystallised solids from a wastewater effluent following the vapourisation of the water phase. It can also be applied as a pre-treatment in order to concentrate the waste stream before thermal exploitation, wastewater incineration or disposal as a hazardous waste. When material recovery is the main objective, a pre-treatment operation prior to evaporation is usually carried out. Examples of pre-treatment include the addition of acids, bases etc. to lower the volatility of molecular compounds, the separation of insoluble, free liquid phases, e.g. oil, and chemical/physical operations to separate heavy metals and/or other solids. Further treatment after evaporation (e.g. incineration) is required, if the concentrate is not recycled. Removal efficiencies as high as 99% have been reported for contaminants which are amenable to treatment by this process (VITO, 2000).

6.14   Stripping

Compounds which possess high volatilities and low water solubilities are amenable to stripping. This is a process in which wastewater is brought into contact with a high gas current flow in order to transfer volatile pollutants from the water phase to the gas phase. Prior to release into the atmosphere, the pollutants must be removed from the stripping gas. This may be achieved by a destructive process or they can be recycled into the process and re-used. The strippability of a compound is more favourable the higher the value of Henry's coefficient, which is the ratio of the vapour phase concentration of the chemical in equilibrium with its concentration in water, and the lower the water solubility. As Henry's coefficient increases with temperature, higher temperatures generally improve air stripping efficiencies, however water evaporation which accompanies the stripping process results in a decrease in the temperature of the wastewater.

The gases which can be used to facilitate the stripping process are air and steam. Air stripping can be operated with or without heating depending on the volatility of the contaminant and when necessary, the heating can usually be supplied from process heat. The most common arrangement within a stripping facility involves a packed tower or column filled with small granules made from polyethylene, stainless steel, polyvinyl chloride or ceramic material which provide the large surface area to volume ratios which increase transfer rates into the air stream. Spray nozzles at the top distribute wastewater over the packing and the stripping gas is fed in a counter-current direction through the packing. A sump at the base collects the decontaminated water (Figure 6.4). The system should be equipped with an air emission control system to prevent the escape of contaminated gases (GAC unit, catalytic oxidiser or incinerator). Steam stripping is an alternative to air stripping and is applied when compounds are less volatile and/or less vulnerable. If a steam generation facility does not exist on the site, this technique may not be economically feasible.
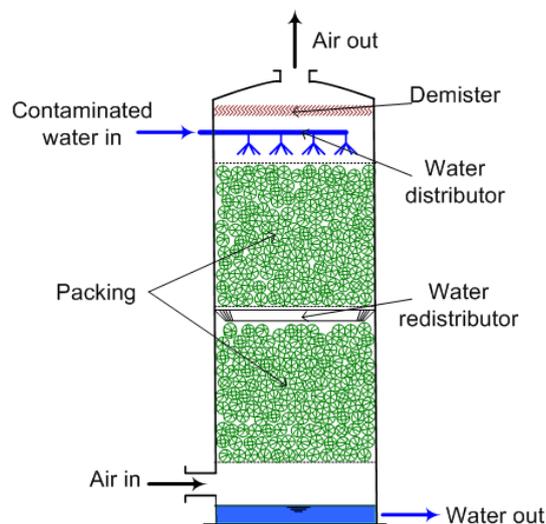
Figure 6-4 Schematic diagram showing the component parts of a countercurrent packed tower for air stripping. (from Wikipedia, http://en.wikipedia.org/wiki/Air_stripping#Air_Strippers).

Strippers can be operated continuously or batchwise, with the latter ensuring consistent performance and higher energy efficiency than continuously operated units. The following contaminants can be separated from wastewaters using the stripping technique:

- chlorinated hydrocarbons, such as trichloroethene, perchloroethene, trichloromethane, dichloroethane and trichloroethane
- ammonia and hydrogen sulphide; because their volatility is strongly dependent on pH, this must be initially adjusted (pH >9.5 for ammonia, pH 2-3 for hydrogen sulphide)
- organic solvents, petrol, diesel fuel, low aromatics, phenol, mercaptans.

The advantages of the stripping technique for separating out the volatile contaminants of wastewaters are the achievement of high removal efficiencies leading to material recovery possibilities with low energy consumption. Disadvantages are that frequent column cleaning is required and the treatment of the downstream gas is essential to eliminate the volatiles removed from the wastewater. This may be more complicated than the stripping operation itself and to ensure an efficient overall treatment, both the stripping stage and the subsequent gas treatment need to be carefully adjusted to each other. The removal of volatile pollutants from the gas phase can be accomplished by:

- adsorption on GAC, zeolite or synthetic resins
- absorption by non-aqueous solvent and subsequent desorption
- absorption by aqueous solutions, such as strong acids (to absorb ammonia)
- condensation or partial condensation and subsequent further treatment
- thermal or catalytic oxidation.

The performance rates achievable by both air and steam stripping for a range of organic and inorganic contaminants are shown in Table 6.11.

6.15   Wastewater Incineration

Wastewater incineration involves the use of elevated temperatures (730 to 1200ºC) and normal pressures to oxidise organic and inorganic contaminants using air and to bring about the simultaneous evaporation of the water content. Lower temperatures can be utilised if catalysts are employed. Typical reaction products are carbon dioxide, water and other inorganic compounds (nitrogen oxides, sulphur oxides, hydrogen halides, phosphates, heavy metal compounds), depending on the contaminants present. In the chemical industry, wastewater incineration can be operated centrally or, as co-incineration, in waste combustion plants. It is only self-sustaining if the organic load is sufficient to ensure adequate energy support for the heating and vaporisation of the water (COD >50 g/l) otherwise a supporting fuel may be required. This can be compensated for by lowering the water content, e.g. by upstream evaporation (see Section 6.12). Wastewater incineration facilities can be either ordinary combustion chambers or fluidised-bed incinerators. Ceramic materials are often used for the internal construction to overcome stability and corrosion resistance problems. Pre-treatment might be necessary to eliminate suspended solids which may result in jet blockage.

Wastewaters which are likely to be subjected to incineration are those containing compounds that are not readily biodegradable, might disturb the biological process in a downstream biological WWTP, or have properties too harmful to be released directly to a sewer system. It is particularly suitable when the contaminants constitute a multi-component mixture with highly variable concentrations and when there is a considerable amount of both organic and inorganic material. Examples are the aqueous residues from dye production and rubber production, aqueous extracts from pesticide production and aqueous residues from polyester production (Ullmann's Encyclopedia of Industrial Chemistry,2000). This technique allows the elimination of pollutants in the presence of high salt concentrations and the generated heat can be used elsewhere within the plant. The produced fly ash has to be disposed of and the incineration of sulphur and/or halide compounds may require flue gas treatment due to the generation of acid gases (e.g. HCl, SO_x).

Table 6-11 Performance efficiencies and emission levels achievable by both air and steam stripping processes

Parameter	Performance rate(%)		Emission level (mg/l)		Remarks
	Air	Steam	Air	Steam	
Ammonia			<5		refinery: low feed concentrations and optimum conditions (examples: sour water stripping)
		99		<50	feed 10 g/l
	>92		70		filtrate from treatment of activated sludge, feed 500-1200 mg/l, feed rate 19-24 m3/h
NH4-N				5	refinery: 2-stage process, feed 1372 mg/l NH4-N
Total inorganic N				7	refinery: 2-stage process, feed 1373 mg/l total inorg. N
Methanol		97			feed rate 3.4 m3/h, concentration 36 g/l
Dichloromethane		99			feed rate 4 m3/h, concentration 5 g
Tetrachloro methane	90-98				packed tower, air/water 5-35:1
1,2-Dichloroethane	65				packed tower, air/water 35:1
Trichloroethene	69-92				packed tower, air/water 4-30:1
	90				spray aeration
Perchloroethene	95				packed tower, air/water 5:1
	90				spray aeration
Hydrocarbons				1.1	refinery: 2-stage process, feed 98 mg/l hydrocarbons
BTX		>99			feed 400 m3/h, concentration 500-1000 mg/l BTX
Hydrogen sulphide			<20		refinery: sour gas stripping
Mercaptans			<20		refinery: sour gas stripping
Phenols		99-99.6		50-200	feed 7-8 m3/h, concentration 20-40 g/l
				0.1	refinery: 2-stage process, feed 182 mg/l phenols
Sulphide				0.5	refinery: 2-stage process, feed 1323 mg/l sulphide
COD				37	refinery: 2-stage process, feed 14400 mg/l COD

(Bundesministerium für Umwelt, 2000; Environment Agency (UK), 1997; Winter, 2000; North Ostrobothnia Regional Environment Centre, 2000)

7. Biodegradable soluble pollutants

Biodegradable wastewater is typically that with a BOD/COD ratio>0.4 (compared to <0.2 for undegradable wastewater) and represents the organic content remaining after the application of physical (see Section 5) and chemical (see Section 6) based treatment techniques. Biological treatment, which may be either centralised or de-centralised, is the degradation of dissolved organic substances by bacteria in the presence or absence of oxygen. Aerobic (oxic) processes use dissolved oxygen whereas anaerobic (anoxic) processes are supported by microorganisms which utilise the biological reduction of oxygen donors to support the biodegradation process. The different characteristics of these processes with respect to their involvement in wastewater treatment are outlined in Table 7.1.

Table 7-1 Comparison of the behaviours of anaerobic, anoxic and aerobic processes during wastewater treatment.

Parameter	Anaerobic	Anoxic	Aerobic
Dissolved oxygen (DO) [mg/l]	0	0	>0
Energy consumption	low	low	high
Sludge production	low	high	high
Sensitivity to toxic substances	high	low	low
COD removal efficiency	<85 %	varying, depending on denitrification	>85 %
Nitrogen removal efficiency	0	45-90 % (nitrification required as first stage)	0
Suitability as pre-treatment	yes	yes	yes
Suitability for last stage treatment	no	no	yes

7.1   Anaerobic Treatment

Anaerobic wastewater treatment results mainly in gaseous products (e.g. methane, carbon dioxide, sulphide etc.) with typically less than 5% of the organic content in the raw effluent appearing in the treated effluent and the excess sludge. The generated biogas consists of about 70% methane, 30% carbon dioxide and other gases such as hydrogen and hydrogen sulphide (VITO, 2000). To ensure the absence of oxygen, the process is carried out in an airtight stirred tank reactor with the microorganisms retained as biomass within the tank. In an anaerobic system there is an absence of gaseous oxygen. The anaerobes access oxygen from sources such as the organic material itself or alternatively from inorganic oxides present in the input material. When the oxygen source in an anaerobic system is derived from the organic material itself, then the 'intermediate' end products are primarily alcohols, aldehydes, and organic acids plus carbon dioxide. In the presence of specialised methanogens, the intermediates are converted to the 'final' end products of methane, carbon dioxide with trace levels of hydrogen sulfide (Fergusen and Mah, 2006). A schematic representation of the different stages involved in a typical anaerobic digestion process is shown in Figure 7.1.

Carbohydratess	⟹	Sugars		Carbonic acids and alcohols	⟹	Hydrogen Acetic acid Carbon dioxide	⟹	Methane Carbon dioxide
Fats	⟹	Fatty acids		Hydrogen Carbon dioxide Ammonia				
Proteins	⟹	Amino-acids						

| Hydrolysis | Acidogenesis | Acetogenesis | Methanogenesis |
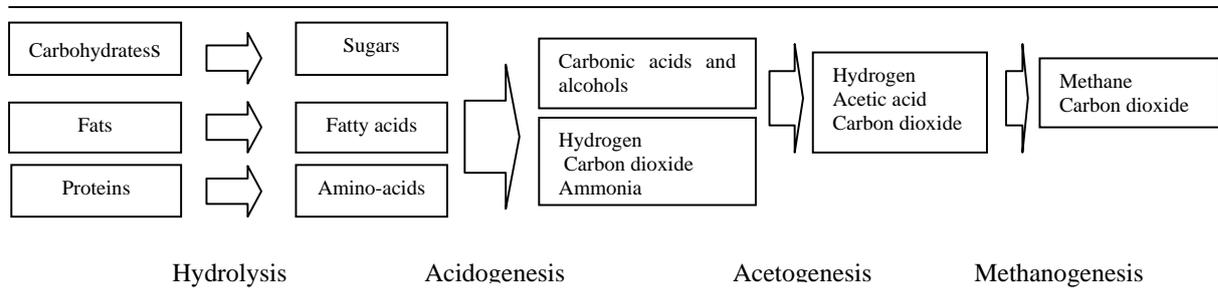
Figure 7-1 The breakdown of carbohydrates, fats and proteins by anaerobic digestion processes.

Anaerobic digestors can operate as batch systems or in continuous mode. The former represent the simplest form in which biomass is added to the reactor at the start of the process in a batch and the system is sealed for the duration of the process. Batch reactors suffer from odour issues that can be a severe problem when they are emptied. Typically, biogas will be produced with a normal distribution pattern over time. Because batch digestion is simple and requires less equipment and lower levels of design work it is typically a cheaper form of digestion. In continuous digestion processes, organic matter is added constantly or in stages to the reactor. The end products are constantly or periodically removed, resulting in constant production of biogas. Examples of reactor designs used for anaerobic digestion include the anaerobic contact reactor (ACR), the upflow anaerobic sludge blanket (UASB), the fixed-bed reactor and the expanded-bed reactor. In the anaerobic contact reactor (see Figure 7.2), wastewater is mixed with recycled anaerobic sludge and digested in a sealed reactor. The wastewater/sludge mixture is externally separated (e.g. by sedimentation, or vacuum flotation) and the supernatant is discharged to the receiving water or sent for further downstream treatment (Metcalf & Eddy, Inc., 1991).
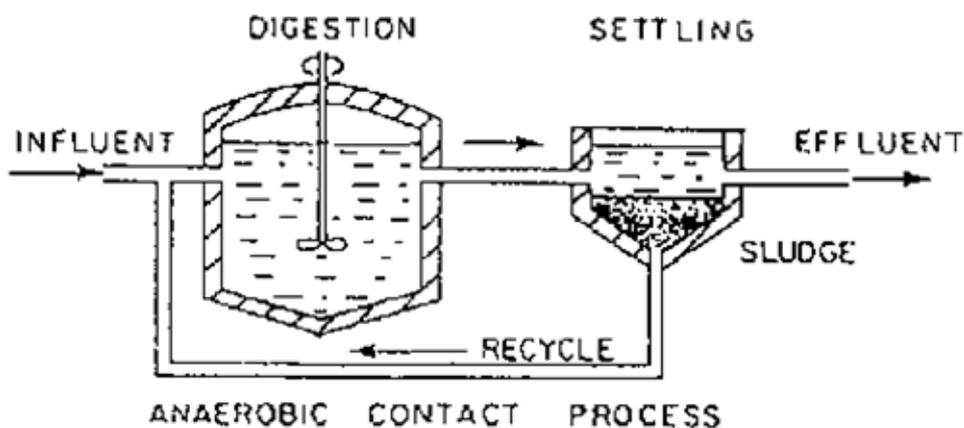
Figure 7-2 A schematic diagram of the anaerobic contact reactor process.

The UASB process utilises a sludge blanket composed of biologically formed granules or particles which is suspended and through which the wastewater flows upwards and is processed by the anaerobic microorganisms (see Figure 7.3). The blanket begins to

reach maturity at around 3 months. Initially, small sludge granules form, whose surface area is covered in aggregations of bacteria and these eventually aggregate into dense compact biofilms referred to as "granules". The produced biogas, containing a high concentration of methane, is collected in domes in the top of the reactor and can be used as an energy source, to heat the digestion tanks. The blanketing of the sludge enables a dual solid and hydraulic (liquid) retention time in the digesters (Metcalf & Eddy, Inc., 1991). Solids requiring a high degree of digestion can remain in the reactors for periods up to 90 days whereas readily biodegradable substances, such as sugars can exit the system in less than a day. UASB reactors are typically suited to dilute waste water streams (3% TSS with particle size >0.75mm).
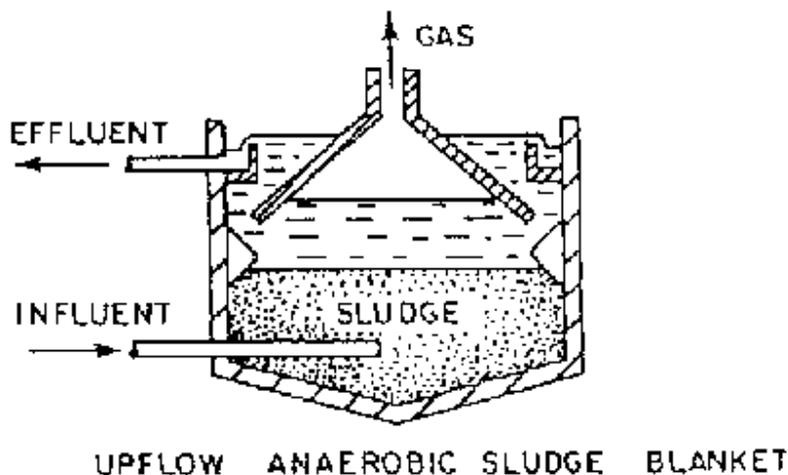
Figure 7-3 Schematic diagram of the UASB process

An expanded granular sludge bed (EGSB) reactor is a variant of the UASB concept but a distinguishing feature is that the wastewater has a faster rate of upward flow through the sludge bed. This increased flux permits partial expansion (fluidisation) of the granular sludge bed, improving wastewater-sludge contact as well as enhancing segregation of small inactive suspended particles from the sludge bed. The EGSB design is appropriate for low strength soluble wastewaters (less than 1 to 2 g soluble COD/l) or for wastewaters that contain inert or poorly biodegradable suspended particles which should not be allowed to accumulate in the sludge bed.

Anaerobic wastewater treatment is mainly used only as a pre-treatment process for wastewaters having high organic loads (>2 gCOD/l) and also exhibiting a uniform quality (Ullmann's Encyclopedia of Industrial Chemistry, 2000). Important advantages over the aerobic treatment of industrial wastewater are lower energy consumption and lower yields of excess sludge (about 10%) requiring disposal. However, a high sensitivity to toxic substances, can lead to increased discharges of activated sludge. There is no stripping of volatile substances and in the presence of sulphate or organic sulphur compounds, heavy metal compounds are converted to sulphides and precipitated. Anaerobic treatment requires temperatures of 20 to 40°C for optimum performance and a pH in the range 6.5 to 7.5. pH values above 8 inhibit the methane forming process. The process has a prolonged start-up which can be partly overcome by 'seeding' from

existing anaerobic bacterial populations. The COD removal rate (normally <85 %) is not sufficient for use as a final treatment stage and therefore further treatment is often required.

The COD removal rate is clearly dependent on the biodegradability of the organic substances which are responsible for the COD content. Examples of the attainable performances of the different types of anaerobic reactors are presented in Table 7.2.

Table 7-2 Performance characteristics of four different types of anaerobic digestion.

Process	Input COD [g/l]	Detention time [h]	Organic loading [kg/(m³ d)]	COD removal [%]
ACP	1.5–5	2–10	0.48–2.40	75–90
UASB	5–15	4–12	4.00–12.0	75–85
Fixed-bed	10–20	24–48	0.96–4.81	75–85
Expanded-bed	5-10	5-10	4.81–9.62	80–85

(Metcalf & Eddy, Inc., 1991)

In combination with downstream aerobic treatment the total performance rates are improved to 99–99.8% removal for BOD and 95–97% for COD.

Anaerobic degradation produces a mixture of methane and carbon dioxide in a ratio of 1-3:1, which represents a combustible gas of high energy content which can be used for fuel replacement or other energy supply facilities. There is a lower energy consumption compared with aerobic processes because there is no energy need for air or oxygen supply to the reactor, only for efficient stirring. Due to the production of combustible gases and the formation of metabolites such as low chain carboxylic acids, closed equipment is essential to prevent the spreading of odours.

7.2   Biological removal of sulphur and heavy metals

This involves a special application of anaerobic treatment which takes advantage of the much lower water solubility of metal sulphides compared to their hydroxides. It is a three-stage process that initially involves the biological conversion of sulphate or other oxidised sulphur compounds to sulphide by means of sulphate-reducing bacteria within a UASB reactor. Reaction of metal ions with sulphide results in the precipitation of the metal sulphides and finally a second biological reaction removes any excess sulphide by converting it to sulphur in a fixed-film reactor (bacteria attached to a suitable carrier material). A tilted-plate settler is employed to separate the sulphur, often in the presence of a suitable flocculant dosage (Paques, 1991).

A COD:sulphate ratio of at least 1:1 is required otherwise electron donors have to be added to support the biological process. Examples of suitable electron donors include hydrogen, starch, ethanol, acetate or propionate esters or salts, and lactate. An application example of this process is the treatment of wastewater from viscose fibre production, where zinc, sulphate and sulphide are the main pollutants. Although the removal of sulphate can occur individually, the reduction of heavy metal content needs enough sulphate to deliver the necessary amount of sulphide for the precipitation reaction.

The performances attainable by this technique are described in Table 7.3 for two metals (zinc and cadmium) and sulphate.

Table 7-3 Biological removal efficiencies for zinc, cadmium and sulphate.

Parameter	Performance rate [%]	Emission level [mg/l]	Remarks
Zinc	99.8	0.05-0.15	influent 100 mg/l
Cadmium	>99	<0.01	influent 1 mg/l
Sulphate	94	75	influent 1170 mg/l, presence of heavy metals

(de Vegt, 1996; Paques, 1991)

The by-products from this treatment process are heavy metal sulphides and sulphur. Depending on the type of metal, the sulphides can be re-used for metal recovery. The sulphur fraction, can be extracted as a sulphur cake, consisting of 60 % dry solids with a purity up to 95 %. This can subsequently be used for the production of sulphuric acid as a feedstock for many industrial chemical processes.

7.3   Aerobic Treatment

Aerobic treatment is the process in which dissolved organic substances are utilised as a food source by microorganisms resulting in their degradation in the presence of oxygen. Oxygen is injected as either air or the pure gas so that the organic components are mineralised into carbon dioxide, water or other metabolites and biomass (the activated sludge). Aerobic wastewater treatment generally represents the final biological step. It offers the advantage of a high rate of sludge growth that not only enables the handling of the various contaminants in wastewater but also provides an efficiency of COD removal that is normally superior to anaerobic treatment. However, the activated sludge is very sensitive to toxicants (e.g. metals, chlorine, cyanide, oils, phenols) resulting in inhibition of the biological process. Threshold toxicity concentrations for chlorine and cyanide are 0.2–1 mg/l and 0.3–2 mg/l, respectively with copper (1-5 mg/l as Cu^{2+}) being representative of several heavy metals. These toxicity levels are subject to conditioning of the microorganisms to the toxicant as they have the ability to adapt to prolonged exposures of low levels of toxic substances (Ullmann's Encyclopedia of Industrial Chemistry, 2000).

Aerobic biological techniques which are used for the treatment of industrial wastewaters include the activated sludge process, the membrane bioreactor process, the trickling or percolating filter process, the expanded-bed process and the biofilter fixed-bed process. The activated sludge process is the most common treatment technique for biodegradable wastewaters generated within the chemical industry. The basic components of this process include an aeration tank, in which the micro-organisms are maintained as a suspension, and into which air (or oxygen) is injected and thoroughly mixed into the wastewater. This is followed by a settling tank (also referred to as a "clarifier") where the waste activated sludge is allowed to settle. Alternatively, the separation can be achieved by air flotation or MF or UF membrane filtration. Part of the waste sludge is recycled to the aeration tank and the remaining waste sludge is

removed for further treatment and ultimate disposal (see Figure 7.4). A further possible modification is a tower design for the aeration chamber, which promotes a higher degradation efficiency because of the smaller air bubbles ascending within a high column of wastewater leading to and increased air/wastewater mass transfer (Ullmann's Encyclopedia of Industrial Chemistry, 2000). In general, CAS is applicable to all biodegradable wastewater streams, whether utilised as high load pre-treatment processes for tributary streams or as the main part of a central WWTP.
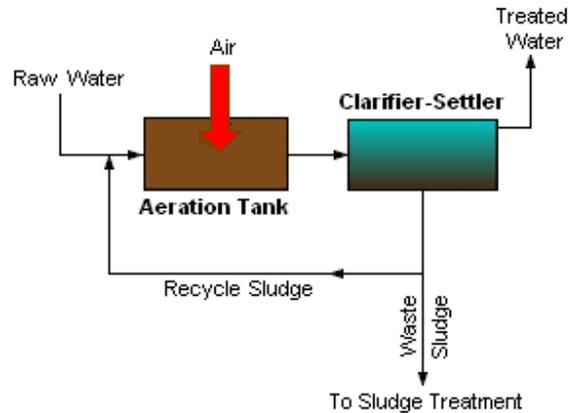
Figure 7-4 Schematic diagram for a conventional activated sludge (CAS) process.

The membrane bioreactor process (MBR) combines activated sludge treatment with a membrane liquid-solid separation process. The hollow fibre membrane component uses low pressure MF or UF membranes and eliminates the need for clarification and tertiary filtration. The membranes are typically immersed in the aeration tank (however, some applications utilize a separate membrane tank). One of the key benefits of MBR is that it effectively overcomes the limitations associated with poor settling of sludge in CAS processes. The membrane fouling problem can be diminished by both aeration and the backwashing of the membrane according to specific conditions adapted for each treatment facility.The technology permits bioreactor operation with considerably higher mixed liquor suspended solids (MLSS) concentration than CAS systems, which are limited by sludge settling. The process is typically operated at MLSS in the range of 8–12 g/L, while CAS are operated in the range of 2–3 g/L. The elevated biomass concentration in the membrane bioreactor process allows for very effective removal of both soluble and particulate biodegradable materials at higher loading rates. This technique has been used to treat industrial wastewaters originating, for example, from the chemical industry, the food processing industry and the pulp and paper industry.

A trickling or percolating filter consists of a fixed bed of rocks, gravel, slag, polyurethane foam, sphagnum peat moss, or plastic media through which the wastewater flows and comes into contact with a layer or film of microbial slime covering the bed media. Aerobic conditions are maintained either by forced air flowing through the bed or natural convection of air if the filter medium is porous. The process mechanisms involve adsorption of organic compounds in the wastewater by the layer of microbial slime, diffusion of air into the slime layer to provide the oxygen required for the biochemical oxidation. As the slime layer builds, it eventually sloughs off into the treated effluent as a sludge that requires subsequent removal and disposal. A representation of a trickling

filter for the treatment of industrial wastewater which incorporates forced aeration is shown in Figure 7.5. Such a treatment system would be used in the chemical industry as part of a central WWTP to reduce the most easily degradable contaminants and to improve the sludge quality in the subsequent aeration stage.
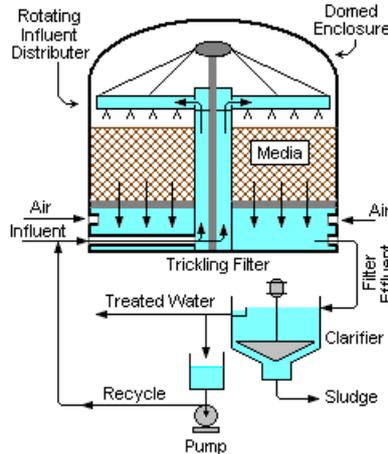
Figure 7-5 A trickling filter system for the treatment of industrial wastewater incorporating forced aeration.

In the biofilter fixed-bed process the biofilm is maintained at the surface of a carrier and as the wastewater passes through the suspended solids are retained in the filter. An example of a suitable carrier material is lignite coke because of its ability to adsorb the organic contaminants, the oxygen and the bacteria material in its pores. The resulting increased reaction time enables refractory COD to be degraded more efficiently than in a CAS process due to a combination of enhanced biodegradation and adsorption on the carrier material. Regular backwashing (typically once a day but dependent on the characteristics of the effluent) is required to maintain the functioning efficiency of the filters. The water flow in a filter is either upflow or downflow and with either sinking or floating medium. Biofilters can have a mono- or multi-layer construction. Whereas multilayer biofilters are fed with raw water without primary settling, monolayer filters are usually used after a primary treatment to remove suspended solids. Biofilters are used to treat industrial effluents which are highly loaded with COD (e.g.in the pulp and paper industry), but also to upgrade existing activated sludge plants. These systems have lower vulnerabilities to high salt contents and can be loaded 2 to 3 times higher than a high-loaded CAS plant and still remove 90% of the COD (INERIS, 2001). The expanded-bed process is operated as described for anaerobic treatment (see Section 7.1) with the distinction that air or oxygen is introduced and aerobic instead of anaerobic bacteria are fixed in the biofilm. The advantage of this version of aerobic treatment is the reduced space requirement with the same performance.

Optimal operation conditions for aerobic systems are dependent on the available nutrient levels. The ideal BOD:N:P ratio is 100:5:1 with critical ratios that should not be exceeded to ensure efficient operation of 32:1 for BOD:N and 150:1 for BOD:P. Wastewater temperatures in excess of 35°C can be critical for aerobic microorganisms and high salt loads (>30 g/l) can cause damage to the microorganisms. The

conventional parameter for gauging the efficiency of biological aerobic treatment is BOD, rather than COD. The latter is a measure of less biodegradable substances which should, ideally, have been considerably depleted by upstream pre-treatment processes. The performance rates of a range of different aerobic process are compared in Table 7.4 for some different regularly monitored parameters.

Table 7-4 Comparison of the performance efficiencies of different aerobic digestion processes.

Parameter	Performance rates [%]				
	CAS	MBR	Trickling filter	Expanded bed	Biofilter fixed-bed
TSS		99			
Turbidity		99			
BOD	85–95	97	40–90 85-95	>98	
COD (TOC)	76–96	>90-96		90	26–68
Phenol index	>99				75–98
AOX					55–98
Total inorganic N		82			4–50
NH4-N		96-98			

(Ullmann's Encyclopedia of Industrial Chemistry, 2000; Metcalf & Eddy, Inc., 1991; North Ostrobothnia Regional Environment Centre, 2000; INERIS, 2001).

7.4 Biological nitrogen elimination

This is achieved by simultaneous nitrification-denitrification involving the overall conversion of the ammonium ions to nitrogen gas in a single bioreactor. In the first stage of nitrification, aerobic microorganisms initially oxidise ammonium to nitrite (e.g. *Nitrosomonas)* which is then further converted to nitrate (e.g. *Nitrobacter*). These autotrophs obtain carbon from CO_2, and use oxygen as the electron acceptor to supply the energy required for the oxidation process. In the subsequent anoxic denitrification stage, heterotrophic organisms convert nitrate to nitrogen gas using carbon from complex organic compounds. In the absence of dissolved oxygen, they use nitrate as the electron acceptor.

The overall process is dependent on floc characteristics, reaction kinetics, mass loading of readily biodegradable organics, rbCOD, and the dissolved oxygen concentration (Tchobanoglous, Burton and Stensel, 2003. As for all biological processes, nitrification-dinitrification is sensitive to toxic substances with 50% reductions in efficiency being caused by inhibition concentrations varying from less than 1 mg/l (e.g. methylamine, dodecylamine) to 500 mg/l (e.g.benzene) (Environment Agency (UK), 1997).

In addition to the common practice of employing two different basins for the autotrophic bacteria and heterotrophic bacteria processes it is possible, through strict control of the dissolved oxygen (DO) levels, to facilitate both nitrification and denitrification in one basin. One way of doing this is to develop an oxygen gradient with decreasing concentrations away from the injection point. In the region of high DO concentration, nitrification and the oxidation of other organic compounds occurs using oxygen as the

electron acceptor. At increasing distances away from the injection point, the reduced DO levels enable heterotrophic bacteria to complete the nitrogen removal. An alternative approach is to produce an oxygen gradient within the bio floc. The DO concentration remains high in the outside rings of the floc where nitrification occurs but low in the inner rings of the floc where denitrification occurs. This method is dependent on the technical ability to control the floc size and their characteristics (Nielson, Thompson and Nielson, 2004). In single basin techniques, the ammonia and nitrate utilization rates are lower than in separate basin designs because only a fraction of the total biomass is participating in either the nitrification or the denitrification steps. Recent research into novel bacteria and system designs has demonstrated that significant ammonia removal can be achieved in an attached growth process with ciliated columns packed with granular sulphur where the denitrifying bacteria use the sulphur as the electron donor and nitrate as the electron acceptor (Hwang, Kim and Choo, 2005). Another well established pathway, used for high ammonia strength wastewater, is the Anammox process using autotrophic denitrifying bacteria (Tchobanoglous, Burton and Stensel, 2003).

Nitrification/denitrification is typically applied to wastewater streams that contain considerable quantities of nitrogen compounds such as amines and ammonium compounds. The process can be incorporated in a central biological WWTP to ensure that ammonium discharge (and possible subsequent conversion to ammonia) does not predicate the receiving water quality. Optimal temperatures are between 12 and 15 °C as lower temperatures restrain the growth of bacteria in the nitrification step. The ideal BOD/N ratio is in the range of 12:1, with the BOD acting as a reducing agent. The levels of total inorganic N received in a feedstock can be reduced by between 70 and 80% with emission levels of 10–20 mg/l.

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PART B: DATABASES FOR INDIVIDUAL PRIORITY POLLUTANTS IDENTIFYING APPLICABLE TREATMENT PROCESSES AND REMOVAL EFFICIENCIES/ACHIEVABLE EMISSION LEVELS.

1. Guidelines for the use of the priority pollutant industrial treatment database

This section of the deliverable contains separate Excel data sheets for 25 priority pollutants arranged alphabetically. Within each data sheet, the production processes and the production activities for the individual pollutants are correlated to emission string identification numbers, which have previously been used in WP3 of this project. From the point of view of treatment, the NOSE-P classifications are of primary importance and, in most cases, these classifications have been clearly matched against previously established emission string numbers. However, there are some instances (e.g. $C_{10} – C_{13}$ chloroalkanes) where it has not been possible to correlate all the production processes against the existing emission string numbers. There are some instances (e.g. chlorpyrifos, diuron and ethylene dichloride) where there are no matches between the existing emission string numbers and the production processes which have been identified as being important in relation to applicable treatment processes.

Within the database it will be observed that on some occasions several NACE classifications have been grouped together and correlated with a NOSE-P classification and an emission string identification. This has been done where a range of production activities can be clearly associated with a specific production process. The emphasis has been placed on production processes as these are of the prime importance when considering the treatment of industrially generated pollutants. There is also column within the database which identifies the possibility for substitution, thereby providing the user with a more complete picture of the possibilities which are available for the control of a particular priority pollutant. The substitution information has been derived from WP 4.1 and in most instances refers to a specific production process (e.g. in the case of benzene) but it may also refer to the different uses of a priority pollutant (e.g.in the case of hexachloro benzene).

Column 9 of the database identifies, using a treatment code(s), a treatment process (or combination of treatment processes) which are relevant for the industrial pollutant under consideration. The treatment codes are fully described in the following section (Section 2) of Part B of this report, where it can be seen that they have been sub-divided into 3 categories according to whether they involve processes appropriate for the removal of suspended solids and insoluble liquids, processes appropriate for the removal of inorganic/non-biodegradable/poorly biodegradable/soluble pollutants or processes appropriate for the removal of biodegradable soluble pollutants (see Part A for a more detailed description). The assignment of industrial treatment techniques relates, where possible, to a particular production process either as a single process or as a combination of processes. However, it has not been possible to identify treatment techniques for all the listed production processes and often the specific treatment techniques are supplemented by the inclusion of 'generic' treatment options, which are

applicable across a range of industrial production processes. Where there is very limited data available, 'generic' treatment options for chemically similar pollutants or pollutant types have also been included. Thus in the case of Endrin, in addition to the 'generic' treatment options for the pollutant itself, 'generic' treatment options for insecticides have been incorporated into the database. Where a cell in the column headed 'Applicable treatment option' has been left blank this indicates that no specific information has been located relating to this aspect. In these situations it is recommended that the 'Generic treatment options' are consulted.

The penultimate column in the database provides identifies the references from which details of the treatment techniques have been obtained. These are primarily the relevant BREF documents as these provide an up-to-date source of the existing Best Available Technology (BAT). Each BREF document is identified by the type of industry that it refers to as well as the associated code. The codes refer to the date of publication (e.g. 08.06 refers to August 2006) and therefore are sometimes replicated. Hence it is important to refer to both the title and the code to fully identify each BREF document. Where it is available, the final information derived from the BREF documents and provided within the database refers to removal efficiencies and/or achievable effluent levels following the treatment process. Unfortunately, there are gaps in the availability of this information and often this is in unexpected areas. Thus, although benzene is extensively used in the chemical industry to manufacture other basic organic chemicals (e.g. ethylbenzene/styrene/polystyrene, cumene/phenol, cyclohexane/nylon, nitrobenzene/aniline/polyurethane and alkylbenzene/surfactants) it has not been possible to find specific information on the applicable treatment processes and the associated treatment efficiencies. Consulting the 'generic' treatment options for benzene, it can be seen that high benzene removal efficiencies can be obtained from relatively high concentration feed streams. Additional information sometimes provided in this topic area refers to the flow rate of the industrial effluent being treated.

In the final three columns of the database, where there are several relevant pieces of information, combinations of single or multiple asterisks have been used to cross-reference between the treatment process, the referenced documentation and the treatment performance. This can be illustrated in the case of cadmium produced during the manufacture of non-metallic mineral products including ceramic products (emission string number; 1460) for which three different treatment processes have been identified. The use of a single asterisk indicates that the use of sand filtration combined with reverse osmosis is able to reduce the concentration of Cd in the effluent from porcelain tableware manufacture from 0.06 mg Cd/l to 0.001 mg Cd/l according to the BREF document on glass manufacture. The same reference identifies a combination of precipitation with settling/sedimentation/clarification as being able to remove 66.7% of Cd from porcelain tableware effluent (marked with a double asterisk). The use of a triple asterisk refers to the BREF document on ceramics which reports that the use of settling/sedimentation/clarification on its own is able to reduce the concentration of Cd in the effluent from the electrical insulator manufacturing process to 0.005 mg/l.

2. Treatment codes allocated to the different industrial techniques

The treatment codes described below are used in the databases in the following section (Section 3) to describe the different treatment processes which can be used either singly or in combination to remove priority pollutants from chemical industry process streams. The categories identified below group the treatment techniques according to their scientific nature such as physical processes (category A), physico-chemical processes (category B) and biological processes (category C).

A. <u>Industrial waste water treatment processes appropriate for the removal of suspended solids and insoluble liquids</u>

   A1. Grit Separation
   A2. Settling/sedimentation/clarification
   A3. Air Flotation
   A4. Filtration
   A5. Microfiltration and ultrafiltration
   A6. Oil-water separation

B. <u>Industrial waste water treatment processes appropriate for the removal of inorganic/non-biodegradable/poorly biodegradable soluble pollutants</u>

   B1. Precipitation
   B2. Crystallisation
   B3. Chemical Oxidation
   B4. Wet Air Oxidation
   B5. Supercritical water oxidation
   B6. Chemical reduction
   B7. Chemical hydrolysis
   B8. Nanofiltration and Reverse Osmosis
   B9. Adsorption
   B10. Ion Exchange
   B11. Solvent Extraction
   B12. Distillation/Rectification
   B13. Evaporation
   B14. Stripping
   B15. Wastewater Incineration

C. Industrial wastewater treatment processes appropriate for the removal of bodegradable soluble pollutants

   C1. Anaerobic Treatment
   C2. Biological removal of sulphur and heavy metals
   C3. Aerobic Treatment

   C4. Biological nitrogen elimination

3. Databases for specific pollutants

In this section, the databases are listed separately for each of the following priority pollutants. Guidelines outlining how the databases can be used have been provided in Section 1 of this part of the report (Part B).

3.1 Anthracene
3.2 Atrazine
3.3 Benzene
3.4 Benzo(a)pyrene
3.5 Cadmium
3.6 Chloroalkanes
3.7 Chlorpyrifos
3.8 Dichloromethane
3.9 Dioctylphthalate (Di(2-ethylhexyl)phthalate (DEHP)
3.10 Diuron
3.11 Endosulphan
3.12 Endrin
3.13 Ethylene dichloride
3.14 Hexachlorobenzene
3.15 Hexachlorobutadiene
3.16 Hexachlorocyclohexane
3.17 Lead
3.18 Mercury
3.19 Nickel
3.20 Nonylphenols
3.21 Pentabromoodiphenylether
3.22 Pentachlorobenzene
3.23 Tributyltin compounds
3.24 Trichloroethylene
3.25 Trifluralin

3.1. Anthracene (CAS No. 120-12-7)

ES no.	Production process	NOSE-P classification	Production activity	NACE classification	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
2381	Characteristic processes in the manufacture of chemicals i.e production /concentration of anthracene	104.09	Manufacture of chemicals and chemical products	24				
2526/2402	Characteristic processes in the manufacture of coke and refined petroleum products leading to release during processing of anthracene oils	104.08	Manufacture of other chemical products	24.6	By-product of the coal tar distillation process and therefore not substitutable			
2382	Preservation of wood during the industrial production of treated wood	107.04.06	Sawmilling and planing of wood; impregnation of wood	20.1	Emissions could be reduced by the introduction of more stringent restrictions on the use of creosote			
2401	Characteristic processes in the manufacture of coke, and refined petroleum products leading to emissions during asphalt production	104.08			By-product of the coal tar distillation process and therefore not substitutable			
2530	Cleaning and washing with water of creosote contaminated skin and/or clothes	112.01.01			Emissions could be reduced by the introduction of more stringent restrictions on the use of creosote			

Generic treatment options (for PAH)	B3; B4; B5; B9 (using GAC)			

3.2. Atrazine (CAS No. 1912-24-9)

ES no.	Production process	NOSE-P classification	Production activity	NACE classification	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
	Pesticide production; chemical installations for the production and formulation of basic plant health products and of biocides	105.09.95	Manufacture of pesticides and other agro-chemical products including insecticides, rodenticides, fungicides and herbicides	24.2	No longer authorised for use in the EU and therefore will disappear from the market	B8*; B9**	Wastewater treatment for the chemical sector (BREF 02.03)	* >70% removal using nanofiltration, 84-97% removal using reverse osmosis; ** 84% removal using GAC for a feed of 0.61 ug/l

			Generic treatment options			B4 (for pesticides); B5 (for organics*)	ditto	* >99%

3.3. Benzene (CAS No. 71-43-2)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
1928	Use of benzene in chemical processes for the production of ethyllbenzene/styrene/polystyrene	107.03.15	Manufacture of other organic basic chemicals	24.14	No substitute; accounts for 52.2% of industrial use in W Europe			
1929	Use of benzene in chemical processes for the production of cumene/phenol	107.03.15	Manufacture of other organic basic chemicals	24.14	No substitute; accounts for 21.5% of industrial use in W Europe			
1930	Use of benzene in chemical processes for the production of cyclohexane/nylon	107.03.15	Manufacture of other organic basic chemicals	24.14	No substitute; accounts for 11.0% of industrial use in W Europe			
1931	Use of benzene in chemical processes for the production of nitrobenzene/aniline/polyurethane	107.03.15	Manufacture of other organic basic chemicals	24.14	No substitute; accounts for 10.8% of industrial use in W Europe			
1932	Use of benzene in chemical processesfor the production of alkylbenzene/surfactants	107.03.15	Manufacture of other organic basic chemicals	24.14	No substitute; accounts for 2.6% of industrial use in W Europe			
1933	Use of benzene in chemical processes for the production of maleic anhydride and others/polyester resins/ plant protection agents	107.03.15	Manufacture of other organic basic chemicals	24.14	No substitute; accounts for 0.8% of industrial use in W Europe			
1936	Use of benzene in chemical processes for the synthesis of products used in the production of insecticides	107.03.15	Manufacture of pesticides and other agro-chemicals	24.2				
1937	Use of benzene in chemical processes for the synthesis of products used in the production of plastics	107.03.15	Manufacture of plastics in primary forms	24.16				
1939	Use of benzene in chemical processes for the manufacture of PCB	107.03.15						

Benzene (continued)

1993	Use of benzene in chemical processes for the manufacture of detergents	107.03.15	Manufacture of soap and detergents, cleaning and polishing preparations	24.51				
1927	Use of benzene for the production of intermediate chemicals	107.03.15	Manufacture of other organic basic chemicals	24.14				
1911	Dye and pigment production	105.09.93	Manufacture of dyes and pigments	24.12				
1935	Synthesis of products used in the production of dyes for paint manufacture	107.03.07	Manufacture of dyes and pigments	24.12				
1972	Manufacture of paints containing benzene	107.03.07	Manufacture of paints, varnishes, and similar coatings, printing ink and mastics	24.3				
1994	Inks manufacturing for the graphic arts industries	107.03.08	Manufacture of paints, varnishes, and similar coatings, printing ink and mastics	24.3				
1997	Printing industry; manufacture of photographic chemicals	107.04.03	Manufacture of photographic chemical material	24.64				
1912	Characteristic processes in the manufacture of rubber, and plastic products, involving fuel combustion	104.1	Manufacture of plastics in primary forms	24.16				
1913	Other polymer, resin and glue manufacturing	105.09.89						
1950	Characteristic processes in the manufacture of textiles and textile products	105.04						

Benzene (continued)

1989	Dry cleaning	107.02.02	Washing and dry-cleaning of textile and fur products	93.01			
1909	Pesticide production	105.09.05	Manufacture of pesticides and other agro-chemicals	24.2			
1982	Characteristic processes in the manufacture of food products, beverages and tobacco	105.03					
1938	Manufacture of pyrotechnic products (explosives)	105.09.97	Manufacture of explosives	24.61			
1914	Use of benzene as a solvent (e.g. For waxes, resins, oils, natural rubber and for general purposes	107.04.13			No universal substitute but toluene has similar properties and is less toxic		
1924	Solvent manufacturing involving the production of benzene	105.09.55	Manufacture of other organic other organic	24.14			
1919	Released during cleaning of pipes when handling crude oil in the production of gas	106	Extraction of crude petroleum and natural gas	11.1			
1921	Petroleum products processing; used as an additive in the production of gasoline	105.08.01	Manufacture of refined petroleum products	23.2			
1944	Characteristic processes in the manufacture of coke, refined petroleum products and nuclear fuel, involving fuel combustion	104.08	Manufacture of coke oven products	23.10		* A6 (API, CPI or SWS) + C3 ** B14 (nitrogen or air) + B9 (GAC) *** B4 (high pressure) **** B5 (373 °C; 221 bar) ***** B3 (low pressure with oxygen) + C3	Refineries (BREF 02.03)	* Pre-treatment (A6) reduces benzene to maximum of 10 mg/l followed by C3 achieving <0.001 to 1 mg/l in effluent ** 1895 l/d of feed at 50 mg/l benzene reduced to , 500 ug/l **** 80% removal efficiency ***** >99.9% removal efficiency

Generic treatment options for benzene		* B9 (GAC) ** B14 (air)	Wastewater treatment (BREF 02.03)	* 95% removal from feed concentration of 1 g/l ** 99% removal from feed rate of 1 m^3/h and concentration of 2 g/l

3.4. Benzo(a)pyrene (CAS No. 50-32-8)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
	Coke oven furnaces	104.08.01	Manufacture of coke oven products (e.g. coke, coke oven gas, lignite tars)	23.1	Produced as an unavoidable by-product of incomplete combustion processes therefore no complete substitution possible	PAH removed by coagulation followed by a) A2 + A4; b) centrifuging +A4; c) A3 + A4; all followed by C3	BREF 12.01 (Iron & steel production)	Levels of benzo(a) pyrene in final effluent should not exceed 0.05 mg/l.
	Other solid fuel transformation (e.g. Involving coal gasification and liquefaction)	104.08.02	Manufacture of coke oven products (e.g. coke, coke oven gas, lignite tars)					
1550	Refinery furnaces (effluents produced)	104.08.03	Manufacture of refined petroleum products	23.2		B14 + C3	BREF 02.03 (Refineries)	< 0.05 mg/l
1569_3	Characteristic processes in the manufacture of basic metals, fabricated metal products and machinery	104.12	Manufacture of basic iron and steel and of ferro-alloys	27.1				
1569_11	Characteristic processes in the manufacture of basic metals, fabricated metal products and machinery	104.12	Aluminium production	27.42				
1569_12	Characteristic processes in the manufacture of basic metals, fabricated metal products and machinery	104.12	Lead, tin and zinc production	27.43				
1569-13	Characteristic processes in the manufacture of basic metals, fabricated metal products and machinery	104.12	Copper production	27.44				
1569_14	Characteristic processes in the manufacture of basic metals, fabricated metal products and machinery	104.12	Other non-ferrous metal production	27.45				
1564_5	Characteristic processes in the manufacture of pulp, paper and paper products, publishing and printing	105.07	Manufacture of paper and paperboard	21.12				
1551	Characteristic processes in the manufacture of textiles and textile products (pre-treatment of fibres)	105.04	Manufacture of textiles	17				

Benzo(a)pyrene (continued)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
1568	Characteristic processes in the manufacture of chemicals, chemical products and man-made fibres	105.09	Manufacture of other organic basic chemicals	24.14				

Specific treatment option for coking plant effluent for PAH	Rotary vacuum drum filter coated with wood flour*; followed by C3**	* 99% removal from an effluent containing 0.7 - 0.8 mg/l; **reduces effluent PAH concentration to <0.15 mg/l
Generic treatment options for PAH	B3; B4; B5; B9 (using GAC)	

3.5. Cadmium (CAS No. 7440-43-9)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
1439	Processes specific to the extraction and distribution of fossil fuels and geothermal energy (coal gasification and liquefaction)	106	Manufacture of coke oven products (coal gasification and liquefaction plants)	23.1		A2	Large combustion plant (BREF 07.06)	Waste water from de-sulpurisation plant contains <0.05 mg Cd/l after treatment
1442_1	Characteristic processes in the maufacture of pulp, paper and paper products, publishing and printing	104.07	Manufacture of pulp	21.11 (also 21.12)				
1444	Characteristic processes in the manufacture of basic metals, fabricated metal products and machinery (emission to water during non-battery production and processing of Cd	104.12	Manufacture of basic metals and fabricated metal products; manufacture of other inorganic basic chemicals	DJ; 24.13	CdS and CdTe used in electronic gates, sensors, switches, detectors, relays and photovoltaic cells; relatively minor uses which are not expected to increase in the future.	B1 combined with A2 or A3 or A4* . B10 **. *** B1 + A2	Speciality inorganic chemicals (BREF 08.07)	* Cd emission levels <0.01 mg/l. ** efficient removal of Cd and its compounds from low feed concentrations. *** Cd efficiently removed from inorganic pigment waste waters
1445	Processes involving use of solvents and other products (surface treatment or products using organic solvents	107	Manufacturing	D	Cd coatings exhibit good corrosion resistanc, high electrical conductivity and high lubricity chracteristics; no replacement with all 3 properties which are necessary for some applications; alloy coatings can be used in some instances	B1 (co-precipitation at pH 9 with Fe(2+)* . B1 (using sulphide) more efficient than hydroxide precipitation and can be followed by A2 or A4. Combinations of technniques e.g. B1 + A2 followed by A5 and/or B8**	Surface treatment of metals (BREF 08.06)	* Achieves Cd emissions in waste waters of <0.1 mg/l (B10 can be used for further clean-up) . ** Achieves very low metal levels in final effluent.
1453	Batteries manufacturing (manufacture of NiCd batteries, accumulators, primary cells, primary batteries	105.13.01	Manufacture of accumulators, primary cells and primary batteries	31.4	NiCd batteries are still widely used but gradual replacement e.g. by Li-ion batteries; NiCd batteries exempted for power tools and industrial uses.			
1456_1	Pharmaceutical products manufacturing	107.03.06	Manufacture of basic pharmaceutical products	24.41 (also 24.42)				

Cadmium (continued)

1457_01-1	Characteristic processes in the manufacture of textiles and textile products (plants for the pre-treatment of fibres and textiles)	105.04	Preparation and spinning of cotton-type fibres	17.11 (also 17.12,17.13, 17.14, 17.15, 17.16, 17.17, 17.21, 17.22, 17.23, 17.24, 17.25, 17.30				
1458	Characteristic processes in the manufacture of basic metals, fabricated metal products	105.12	Manufacture of fertilisers and nitrogen compounds	24.15				
1459	Characteristic processes in the manufacture of basic metals, fabricated metal products	105.12	Manufacture of other inorganic basic chemicals	24.13				
1460	Characteristic processes in the manufacture of other non-metallic mineral products	105.11	Manufacture of other non-metallic mineral products cement, klinker, lime, mineral substances or ceramic products)	26.5	Cd based pigments used because of their stability during high temperature processing; alternatives available for low temperature processes; CeS only current substitute for high temperature pprocesses.	A4 (sand) + B8 (Reverse Osmosis)* ; B1 + A2**; A2 only***	Glass manufacture (BREF 12.01) *, **, ***Ceramics (BREF 08.07)	Cd water emissions typically <0.05 mg/l after treatment *Effluent from porcelain tableware manufacture (0.06 mg Cd/l) reduced to 0.001 mg Cd/l) **>66.7% removal of Cd from porcelain tableware effluent *** effluent from electrical insulator manufacture reduced to 0.005 mg Cd/l
1464	Slaughter houses	105.03.42	Production and preserving of meat	15.11				

Cadmium (continued)

1493_01	Characteristic processes in the manufacture of basic metals, fabricated metal products (metal ore roasting installations; installations for the production of ferrous and non-ferrous metals [Zn mining, PB and Zn refining, Cd metal and non-ferrous metal])	105.12	Manufacture of basic iron and steel and of ferro-alloys	27.10 (also 27.31, 27.32, 27.33, 27.34, 27.51, 27.52, 27.52, 27.54, 27.41, 27.42, 27.43, 27.44, 27.45	Many brazing and soldering alloys have been substiuted for Cd; currently substitution has not been possible in Cu-Cd and Cu-Cd-Ti thermal and electriucal conductivity alloys; Ag-Cdo electrical contact alloys; 'Ni brazing alloys' containing Cd	B1 + neutralisation + A4 (sand) * ; A2 + cooling + A4 (sand) ** ; B1 (using lime and iron sulphate) + A2***	* Iron and Steel production (BREF 12.01) ** Ferrous metal processing (BREF 12.01) ***Non-ferrous metal processes (BREF 12.01)	* Sinter plant waste water emissions of Cd <0.1 mg/l ** Hot rolling mill waste water Cd emissions <0.1 mg/l *** Primary and secondary Copper process waters reduced to 0.1 mg Cd/l
1746_1	Characteristic processes in the manufacture of food products, beverages and tobacco	105.03	Processing and preserving of potatoes	15.31 (also 15.32, 15.33,15.41, 15.42,15.43				
			Generic treatment options for Cd			A2	Wastewater treatment (BREF 02.03)	98% removal
						B1	ditto	Performance dependent on situation
						B8	ditto	Nanofiltration achieves >90% removal
						B9	ditto	Using zeolites as adsorbent
						B10	ditto	Cation exchangers (Na) give good removal of Cd and compounds at low feed concentrations
						C2	ditto	>99.8% removal when sufficient sulphate present to support sulphide formation; emission levels <0.01 mg/l from influent of 1 mg/l.

Specific treatment option for electroplating wastewaters	Electrodialysis and Reverse Osmosis widely used for soluble Cd	Non-ferrous metal processing (BREF 12.01)	>99.8% removal

3.6. Chloro-alkanes; C$_{10}$ – C$_{13}$ (CAS No. 8535-84-8)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
1438	Characteristic processes in other manufacturing, involving fuel combustion; release during production of basic organic chemicals (production of SCCPs). Large industrial point sources, direct or via STP (IPPC installations)	104.13	Manufacture of other organic basic chemicals	24.14	Possible substitutes according to identified use are listed below. Many of the suggested replacements may themselves cause environmental problems and therefore a closed production is recommended as a risk reduction measure. Metal working fluids - MCCPs; LCCPs; alkyl phospate esters Paint plasiticisers - MCCPs; LCCPs; Various esters; phophate; boron containing compounds Sealants - MCCPs; LCCPs; phthalate esters Leather industry - LCCPs; natural animal and vegetable oils. Flame retardant in rubber, textiles and PVC - anitimony trioxide; alumimium hydroxide; acrylic polymers; phospates.	B14 (steam or hot air)	Large volume organic chemicals (BREF 02.03)	Chlorinated organic compounds reduced to concentrations < 1 mg/l; off-gases passed to condensation (for recovery) or incineration
1454_1	Rubber production (non-solvent processes); release during use as flame retardant in rubber formulations	105.10.01	Manufacture of rubber tyres and tubes and other rubber products	25.11; 25.12; 25.13				
1467_01	Characteristic processes in the manufacture of leather and leather products; release during use of chemical mixture for leather production	104.05	Tanning and dressing of leather; manufacture of leather products	19.10; 19.20; 19.30		B14 + B9 (GAC)	Tanning of hides and skins (BREF 02.03)	Halogenated hydrocarbons removed from tannery wastewater
1471_01	Characteristic processes in the manufacture of basic metals, fabricated metal products and machinery; release during use in metal working and extreme pressure lubricating fluids	104.12	Manufacture of basic iron and steel and of ferro-alloys; other metal production; fabricated metal products	27.10; 27.21; 27.22; 27.31; 27.32; 27.33; 27.34; 27.41; 27.42; 27.43; 27.44; 27.45; 28.11; 28.40		B9 (GAC)	Non-ferous metal processes (BREF 12.01)	Removal of >99.5% of chlorinated hydrocarbons

Chloro-alkanes; C$_{10}$ – C$_{13}$ (CAS No. 8535-84-8) (continued)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
1471_01 (continued)	Production of paints and coatings; used as a plasticiser/flame retardant	104.12	Manufacture of basic iron and steel and of ferro-alloys; other metal production; fabricated metal products	27.10; 27.21; 27.22; 27.31; 27.32; 27.33; 27.34; 27.41; 27.42; 27.43; 27.44; 27.45; 28.11; 28.40	As above			
	Production of sealants and adhesives; used as a plasticiser/flame retardant							
	Textile applications; waterproofing agent							
	Mineral oil and gas refineries							
	Basic inorganic chemicals and fertilisers							

Generic treatment options			Biological treatment achieves final chlorinated hydrocarbon concentration of 1 mg/l; extended aeration can remove 85-95% of COD.
	C1/C3		

3.7. Chlorpyrifos (CAS No. 2921-88-2)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
	Pesticide production	105.09.95	Manufacture of pesticides and other agro-chemical products	24.2	Used as an insecticide for locust control, termites, cockroaches, mosquitoes; very important for control of potato wireworm and scale in citrus culture for which substitution would result in increased levels of resistance development and currently not feasible.	B8 (reverse osmosis)*; B9 (PAC)**	Common waste water treatment in the chemical sector (BREF 02.03)	Quoted efficiencies are for fenitrothion which has a similar chemical structure to chlopyrifos; * 99% ** 99%

Generic treatments for insecticides		B14 + B3 (ozone) + C3	Organic fine chemicals (BREF 08.06)	
		B4 + B15 + C3	ditto	
		B7 (under pressure)	ditto	
		B11	ditto	
		B9 (GAC)	ditto	

3.8. Dichloromethane (CAS No. 75-09-2)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
2070	Wastewater treatment following use a solvent in coffee extraction	109.02	Processing of tea and coffee	15.86	Substitutes for paint stripping are n-methyl-2-pyrrolidone; benzyl alcohol; dimethyl suphoxide; 1,3-dioxane; sodium hydroxide; dibasic esters, mechanical stripping; thermal stripping. Substitutes as a solvent dependent on nature of substance to be dissolved/extracted. Aerosol use supported by lack of impact on ozone layer and non-flammability			
2181	Pharmaceutical products manufacturing (used as a solvent)	107.03.06	Manufacture of basic pharmaceutical products	24.41				
2183	Paints manufacturing (used as a paint stripper/remover)	107.03.07	Manufacture of paints, varnishes and similar coatings, printing ink and mastics	24.3				
2184	Inks manufacturing (used as stripper/remover)	107.03.08	Manufacture of paints, varnishes and similar coatings, printing ink and mastics	24.3				
2186	Metal degreasing (in aluminium forming industry)	107.02.01	Aluminium production	27.42				
2189	Electronic components manufacturing (solvent in manufacture of photographic equipment and supplies	107.02.03	Manufacture of optical instruments and photographic equipment	33.4				
2190	Rubber processing (used as solvent)	107.03.05	Manufacture of rubber tyres and tubes	25.11				
2193	Characteristic processes in the manufacture of rubber and plastic products, involving fuel combustion (solvent in organic chemical/plastics processing)	104.1	Manufacture of plastic plates, sheets, tubes and profiles	25.21				

Dichloromethane (CAS No. 75-09-2) (continued)

Generic treatment options for dichloromethane	B14 (air)	Wastewater treatment in the chemical sector (BREF 02.03)	99% removal at a feed rate of 1 m³/h and concentration of 2 g/l.
	B14 (steam)	ditto	99% removal at a feed rate of 4 m³/h and concentration of 5 g/l.
Generic treatment options for AOX	B3	ditto	80% removal ((using chlorine/hypochlorite at a feed rate of 40 mg/l AOX
	B4	ditto	80% removal (at 280°C and 12 Mpa)
	B9 (GAC)	ditto	>90% removal using a moving bed adsorbent configuration at a feed rate of 60 mg/l)
	C3	ditto	55-98% removal in a fixed-bed biofilter
Generic treatment options for chlorinated solvents	B9	ditto	
Generic treatment options for organics	B5	ditto	99% removal

3.9. Dioctyl phthalate or Di(2-ethylhexyl)-phthalate (DEHP) (CAS No. 117-81-7)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
1422	Characteristic processes in the manufacture of other non-metallic mineral products (non-polymer products; mainly sealants and inks, also paint and ceramics)	105.11	Manufacture of other non-metallic mineral products	26	>90% of the DEHP produced is used in the production of flexibles PVC - possible substitutes are di(isononyl)			
1446	Characteristic processes in the manufacture of rubber and plastic products, involving fuel combustion (use of DEHP as plasticizer in polymers 97-98% (mainly PVC); release during industrial use as polymer - formulation and processing; extrusion compound)	104.1	Manufacture of other chemical products n.e.c.	24.66				
1447_1	Other polymer, resin and glue manufacturing (use of DEHP as plasticizer in polymers 97-98% (mainly PVC); other polymer manufacturing; release during industrial use as polymer - formulation and processing; calendering.	105.09.89	Manufacture of explosives; glues and gelatins; essential oils; photographic chemical material; prepared unrecorded material; other chemical products	24.61; 24.62; 24.63; 24.64; 24.65; 24.66				
1448	Polyvinylchloride (manufacture of plastic plates and sheets; use of DEHP as plasticizer in polymers 97-98% (mainly PVC); release during industrial use as polymer - formulation and processing; plastisol spread coating	105.09.82	Manufacture of plastic plates, sheets, tubes and profiles; plastic packing goods; builders ware of plastic; other plastic products	25.21; 25.22;25.23; 25.24				
1449	Characteristic processes in the manufacture of rubber and plastic products, involving fuel combustion (use of DEHP as plasticizer in polymers 97-98% (mainly PVC); release during industrial use as polymer - formulation and processing; extrusion compound)	104.1	Manufacture of plastic plates, sheets, tubes and profiles; plastic packing goods; builders ware of plastic; other plastic products	25.21; 25.22;25.23; 25.24				
1462_6	Characteristic processes in the manufacture of chemicals, chemical products and man-made fibres, involving fuel combustion (release during manufacture of organic basic chemicals; release from production of DEHP at production site).	104.09	Manufacture of other organic basic chemicals	24.14				

Generic treatment options for DEHP		C3	78-94% removal; the lower value corresponds to a5 mg/l feed
Generic treatment options for organic compounds		B5	>99%

3.10. Diuron (CAS No. 33-54-1)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
	Pesticide production; chemical installations for the production and formulation of basic plant health products and of biocides	105.09.95	Manufacture of pesticides and other agro-chemical products including insecticides, rodenticides, fungicides and herbicides	24.2	No longer authorised for use in the EU and therefore will disappear from the market	B9 (GAC)	Organic fine chemicals (BREF 08.06)	Followed by recycling of most of the mother liquor

| | Generic treatment options | | | | | B4 (for pesticides); B5 (for organics*) | | * >99% |

3.11. Endosulphan (CAS No. 115-29-7)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
2095	Pesticide production	105.09.95	Manufacture of pesticides and other agro-chemical products	24.20	Use as an insecticide, wood prervative and acaricide to be banned from 31/12/07			
2096	Preservation of wood	107.04.06	Sawmilling and planing of wood; impregnation of wood	20.10				

Generic treatment options for endosulphan	B4	Wastewater treatment in the chemical sector (BREF 02.30)	98.4% removal; endosulphan reduction from 18.4 mg/l to 0.29 mg/l.
	C3		90% removal increasing to 96% following acclimatisation
Generic treatment options for insecticides	B14 + B3 (ozone) + C3	Organic fine chemicals (BREF 08.06)	
	B4 + B15 + C3	ditto	
	B7 (under pressure)	ditto	
	B11	ditto	
	B9 (GAC)	ditto	

3.12. Endrin (CAS No. 72-20-8)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
2441	Pesticide production	105.09.05	Manufacture of pesticides and other agro-chemical products	24.20	Endrin is no longer manufactured in the EU and its uses are banned; previously used as an insecticide to protect crops			

Generic treatment options for endrin	A2 (following coagulation)	Wastewater treatment in the chemical sector (BREF 02.03)	43% removal
	B4 (high pressure)	ditto	>97% removal from a feed of 3.6 mg/l.
	B9 (PAC)	ditto	>99.9% removal at afeed of 0.01 mg/l; using PAC at a concentration of 70 mg/l
Generic treatment options for insecticides	B14 + B3 (ozone) + C3	Organic fine chemicals (BREF 08.06)	
	B4 + B15 + C3	ditto	
	B7 (under pressure)	ditto	
	B11	ditto	
	B9 (GAC)	ditto	

3.13. Ethylene dichloride or 1,2-Dichloroethane (DCE) (CAS No.: 107-06-02)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
	Production of DCE	105.09.57; 105.09.59	Manufacture of basic chemicals	24.1				
	Production of vinyl chloride followed by PVC	105.09.58; 105.09.59	Manufacture of basic chemicals	24.1	Not economically feasible	B14 (at atmos press.; under press; or under vacuum)* ; other options include B14 + C3 and B9 + A2	Large volume organic chemicals; 02.03 (p 357)	* 65% removal using air stripping within a packed tower configuration and employing an air/water ratio of 35:1; EDC effluent concn < 1 mg/l
	Production of ethylene diamine (+ ethylene polyamine	105.09	Manufacture of basic chemicals	24.1	Reaction between DCE and ammonia not replacable			
	Production of 1,1,1-trichlo-ethane, trichloro-ethylene and perchloro-ethylene	105.09.62	Manufacture of basic chemicals	24.1	Alternative synthetic routes exist			
	Extraction solvent (in pharmaceuticals and basic organic chemicals industries)	107.04	Manufacture of chemicals and chemical products	24	No universal substitute available			
	Cleaning/degreasing agent for metals	107.02.01	Manufacture of basic metals and fabricated metal products	DJ	Possible substitution by chlorinated solvents (also PPs) or oxygenated solvents			

Specific treatment options	B8		71% removal achievable by nanofiltration
Generic treatment options for AOX	B3; B4; B5; B11; B12		

3.14. Hexachlorobenzene (CAS No. 118-74-1)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
2101	Production of halogenated hydrocarbons (by-product)	105.09.60	Manufacture of other basic chemicals	24.14	Not produced within the EU but still occurs as an unavoidable by-product from the chlorine industry, cement and ceramic production, secondary aluminium industry and waste incineration plants 2102	. B14 (steam or hot air) + C3	Large volume organic chemicals (BREF 02.03)	Initially, effluent reduced to < 1mg/l (B14) and then 0.001 mg/l (as hexa- and penta-chlorobenzenes)
2102	Pesticide production	105.09.95	Manufacture of pesticides and other agro-chemical products	24.20				
2105	Alumina production (by-product)	104.12.13	Aluminium production	27.42				
2106	Manufacture of pyrotechnic products (fireworks, military products)	105.09.97	Manufacture of other chemical products n.e.c.	24.66; 24.61				
2110	Preservation of wood (impurity of PCP)	107.04.06	Sawmilling and planing of wood; impregnation of wood	20.10				
2111	Characteristic processes in the manufacture of textiles and textile products (impurity of PCP)	105.04						

Generic treatment options for HCB	A2 (following coagulation)	Wastewater treatment in the chemical sector (BREF 02.03)	59%

3.15. Hexachlorobutadiene (CAS No. 87-68-3)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
2117	Refinery furnaces (emission from mineral oil and gas refineries)	104.08.03	Manufacture of refined petroleum products	23.20	Not produced anymore in the EU. However, it occurs as an unintentional, unavoidable by-product from the chlorine industry and production of basic organic chemicals			
	Production of halogenated hydrocarbons (by-product)	105.09.60	Manufacture of other organic basic chemicals	24.14		B14 (steam or hot air) + C3	Large volume organic chemicals (BREF 02.03)	Initially, effluent reduced to < 1mg/l (B14) and then 0.001 mg/l (as hexachlorobutadiene)

3.16. Hexachlorocyclohexane (CAS No. 608-73-1)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
2121	Preservation of wood	107.04.06	Sawmilling and planing of wood; impregnation of wood	20.10	The gamma isomer used as an insecticide for forest pests, fumigating storage rooms and disinfection; agricultural use banned in the EU; can be substituted by pyrethoids			
2123	Pesticide production	105.09.95	Manufacture of pesticides and other agro-chemical products	24.20				
2124	Refinery furnaces (emission from mineral oil and gas refineries)	104.08.03	Manufacture of refined petroleum products	23.20				
			Generic treatment options for lindane			B8 (reverse osmosis)	Wastewater treatment for the chemical sector (BREF 02.03)	99%

3.17. Lead (CAS No. 7439-92-1)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
2128	Production processes in manufacturing industry and water supply (lead used as raw material for synthesis, in electrolyses and in stabilisers in Sweden	105						
2146	Electronic components manufacturing (eg. major use of tin-lead alloys in electronics industry)	107.02.03	Manufacture of electronic valves and tubes and other electronic components	32.10	Lead free alloys to replace solder exist (eg. tin-silver-copper) but are more brittle; all electronic products sold in the EU must be lead free			
2150	Paints manufacturing (lead pigments e.g. lead chromate; also used as drying agents)	107.03.07	Manufacture of paints, varnishes and similar coatings, printing ink and mastics	24.30	Replacements are possible for use as pigments (inorganic and organic dyes); corrosion inhibitors (zinc phosphate; zinc oxide/iron oxide); drying agents (zirconium or calcium compounds)	B1 (following neutralisation) + A2 (following flocculation) + A4	Speciality inorganic chemicals (BREF 08.07)	Discharge Pb level <0.5 mg/l
2153	Polyvinyl chloride processing) lead salts used as stabilisers)	107.03.02			Possible substitutes for lead stearate, sulphate or phosphate as stabilisers are calcium/zinc and barium/zinc stabilisers			

Lead (continued)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
2156	Characteristic processes in the manufacture of other non-metallic mineral products	105.11	Manufacture of glass and glass products; manufacture of ceramic goods (eg. leaded glass containing lead oxide; radiation shielding glass; cement clinkers; lime glass)	26.10; 26.20	Possible lead substitutes in crystal glass include metals such as bismuth, barium, strontium, zinc and titanium	* Glass manufacture: a) B1 (using calcium carbonate) + A2 b) A4 ** Ceramics manufacture a) A4 (sand) + B8 (reverse osmosis) b) A2 (after flocculation)	* Glass manufacture (BREF 12.01) ** Ceramics (BREF 08.07)	* a) Removal of soluble Pb sulphate formed during acid dipping of glass to <0.5 mgPb/l b) removal of fine glass particles ** a) Pb in porcelain tableware effluent reduced from 250 mg/l to 0.06 mg/l (by A4) and <0.01 mg/l by additional B8 (overall removal >99.99%) b) Pb in electrical insulator effluent reduced to <0.05 mg/l
2211	Batteries manufacturing	105.13.01	Manufacture of accumulators, primary cells and primary batteries	31.40	No ready replacement for use of lead in batteries			
2218	Characteristic processes in the manufacture of basic metals, fabricated metal products and machinery	104.12	Lead, zinc and tin production	27.43	Difficult to replace lead as sheathing for electrical cable but in futurewill be confined to marine applications; lead weights for wheel balancing can be replaced by tin, tungsten and a zinc-aluminium-copper alloy.	* B1 (lime or iron sulphate) + A2 ** B1 (sodium hydrogen sulphide) + A2 + A4 (sand) *** B1 (combined hydroxide/sulphide) + A2	Non-ferrous metal processes (BREF 12.01)	* Pb in Cu process water reduced from 500 mg/l to 0.2 mg/l; >99.9% removal ** Pb in Cu process water reduced from 500 mg/l to 0.04 mg/l; >99.99% removal *** Pb in wastewater from Pb and Zn production reduced to <0.1 mg/l
2219	Combustion processes (production of heat and electricity)	101	Production and distribution of electricity	40.10		A4 + B1 + A2 + neutralisation (B10 may also be used)	Large combustion plant (BREF 07.06)	Pb removed from wastewater arising from wet FGD to < 0.1 mg/l
2222	Characteristic processes in the manufacture of chemicals, chemical products and man-made fibres	105.09	Manufacture of other inorganic basic chemicals (phamaceuticals; cacium carbide; biocides; fertilisers)	24.13				

Lead (continued)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
2227	Characteristic processes in the manufacture of pulp, paper and paper products, publishing and printing	105.07						
2228	Characteristic processes in the manufacture of textiles and textile products	105.04	Finishing of textiles	17.3				
2232	Processes involving use of solvents and other products	107						
2246	Refinery furnaces	104.08.03	Manufacture of refined petroleum products	23.20				
2252	Characteristic processes in the manufacture of chemicals, chemical products and man-made fibres	105.07				B1 (using Na hydrogen sulphide) + A2 (centrifuging)	Large volume organic chemicals (BREF 02.03)	Pb removal during adiponitrile manufacture
2254	Characteristic processes in the manufacture of chemicals, chemical products and man-made fibres	105.09	Manufacture of other chemical products n.e.c.	24.66		Pb azide* and Pb trinitroresorcinate** in explosives manufacture: convert to Pb nitrate followed by B1 (using sulpuric acid or Na carbonate)	Speciality inorganic chemicals (BREF 08.07)	* 1500 mg Pb/l reduced to 5 mg Pb/l ie. 99.7% removal ** 30000 mg Pb/l reduced to 15 mg Pb/l ie. 99.9% removal

	Generic treatment options					B1 (using either lime, dolomite, Na hydroxide, Na carbonate, sulphide) + A2	Wastwater treatment for the chemical sector (BREF 02.03)	

3.18.   Mercury (CAS No. 7439-97-6)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
1539	Characteristic processes in the manufacture of coke, refined petroleum products and nuclear fuel, involving fuel combustion	104.08	Manufacture of coke oven products; refined petroleum products	23.1; 23.2				
1541	Coke oven furnaces	104.08.01	Manufacture of coke oven products	23.10				
1542	Characteristic processes in the manufacture of food products, beverages and tobacco	105.03	Manufacture of food products and beverages	15				
1543	Characteristic processes in the manufacture of textiles and textile products	105.04	Manufacture of textiles	17				
1545	Batteries manufacturing	105.13.01	Manufacture of accumulators, primary cells and primary batteries	31.4	Mercuric oxide and mercury zinc batteries can be substituted by zinc-air batteries (virtually Hg free) and lithium cells; All other mercury based standard and rechargeable batteries can be replaced by Hg-free versions	* B10 (Superlig process) ** B1 (KI) produces HgI_2	Non-ferrous metal processes (BREF 12.01)	* <0.5 mg Hg/l discharged
1546	Pesticide production	105.09.95	Manufacture of pesticides and other agro-chemical products	24.2				

Mercury (continued)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
1547	Characteristic processes in the manufacture of chemicals, chemical products and man-made fibres	105.09	Manufacture of basic chemicals; other inorganic basic chemicals; fertilisers and nitrogen compounds; emission from chlor-alkali industry	24.1; 24.13; 24.15; 24	Mercury cell process can be substituted by membrane technology or non-asbestos diapragm technology.	* B1 (hydrazine) + A2 + A4 (sand) + B9(GAC) ** B1 (NaHS) + A2 *** A2 + B10 **** B3 (Cl_2 ; to produce Hg_2Cl_2) + B10	Chlor-Alkali manufacture (BREF 12.01)	* 99.8% removal from waste flow of 7 m^3/h ** 4ug Hg/l discharges from waste flow of 15 m^3/h *** 50 ug Hg/l discharged from waste flow of 8 m3/h **** <5 ug Hg/l discharged
1548	Pharmaceutical products manufacturing	107.03.06	Manufacture of pharmaceuticals, medicinal chemicals and botanical products	24.4				
1563_1	Characteristic processes in the manufacture of pulp, paper and paper products, publishing and printing	105.07	Manufacture of pulp; paper and paperboard	21.11; 21.12	Unavaoidable by-product due to Hg in raw materials - requires emission control.			
1584_1	Extraction of metal ores	105.02.02	Mining of non-ferrous metal ores, except uranium and thorium ores; iron ores	13.20; 13.10	Hg used in extraction of gold in some countries - can be avoided but not widely accepted.			
1696	Combustion plants >= 50 and < 300 MW (boilers)	101.02	Production and distribution of electricity	40.1	Unavaoidable by-product - requires emission control			
1698	Characteristic processes in the manufacture of other non-metallic mineral products, involving fuel combustion	104.11	Manufacture of other non-metallic mineral products	26				

Mercury (continued)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
1701	Characteristic processes in the manufacture of basic metals, fabricated metal products and machinery	104.12	Manufacture of basic metals	27	Hg use in thermometers can be replaced by other liquids or gasesor bt electrical or electronic sensors; use as a 'heavy liquid' in pressure gauges, pressure switches and pressure transmitters can be substituted;Hg in electrical or electronic components can be replaced.			

Generic treatment options for Hg				Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
Generic treatment options for Hg				A2 (following coagulation)	Wastewater treatment (BREF 02.03)	70% removal
				B1(Na_2S or polyorganosulphides) + A2	ditto	
				B1(Na_2S or polyorganosulphides) + A3	ditto	
				B1(Na_2S or polyorganosulphides) + A4 (sand)	ditto	Emission level of 50 ug Hg/l
				B1(Na_2S or polyorganosulphides) + A5	ditto	
				B8 (NF)	ditto	>90% removal of inorganic or organic Hg
				B9 (GAC)	ditto	>90% removal of inorganic or organic Hg from a feed of 29 ug/l

3.19. Nickel (CAS No. 7440-02-0)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
2264	Release during manufacturing processes due to the use of Ni as a catalyst for chemical reactions (e.g. used as hydrogenation catalyst, methanation catalyst etc). Released in process water.	112.02.03			No ready replacement to use of Ni as a hydrogenation catalyst	* A4 + B10 ** B1 + A4 *** Destruction of heavy metal complex with Na dithionate + B1 + A4	Organic fine chemicals (BREF 08.06)	Discharged effluent values: * <0.5 mg/l ** 0.49 mg/l *** 0.1 mg/l
2404	Extraction of metal ores; release during surface mining for nickel production - primary extraction phase	105.02.02	Mining of metal ores	13				
2406	Characteristic processes in the manufacture of basic metals, fabricated metal products	105.12	Manufacture of basic iron and steel and of ferro-alloys	27.10; 27.21;27.22; 27.42; 27.45; 27.51; 27.52; 27.54; 28.51	No current replacement for Ni in stainless steel and other alloys e.g with Cu	* B1 + neutralisation + A4 (sand) ** A2 (after flocculation with Al sulphate or polymers) *** A2 + A4 or A3 or B1 (flocculation) **** A2 + flocculation + A4 (sand)	Iron and steel production (BREF 12.01) and Ferrous metal processing (BREF 12.01)	Discharged effluent values: * <0.1 mg/l ** 0.02 mg/l *** <0.2 mg/l **** 0.07 mg/l
2418	Extraction and 1st treatment of solid fossil fuels; release of Ni from coal and other energy producing materials during excavation/transport/processing	106.01		C.CA				
2425	Nickel production; release during Class1 Ni production.	105.12.26	Other non-ferrous metal production	27.45		* A2 + neutralisation + B1 + A4 ** B1 (lime or Fe sulphate) + A2 *** B1 (NaHS) + A2 + A4 (sand)	Non-ferrous metal processes (BREF 12.01)	Discharged effluent values * <0.1 mg/l ** 0.5 mg/l *** 0.07 mg/l

Nickel (continued)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
2436	Characteristic processes in the manufacture of other non-metallic mineral products	105.11		D.DI		A2 (following flocculation)	Ceramics (BREF 08.07)	Discharged effluent concentration <0.1 mg/l
2438	Recovery of paper and paperboard	105.14.26		37.2				
2462	Manufacture of metal constructions/articles; release during industrial processes such as electroforming, electroplating, electrotyping	105.12.81	Manufacture of fabricated metal products, except machinery and equipment	28	No ready replacement to nickel-plating	Neutralisation + B1 + A4 (gravel) + B10		> 99.95% removal
2473	Leakage and spillage from equipment; release of Ni due to runoff from stainless steels used for maufacturing industry applications - i.e. production lines and machinery parts	112.09.12	Manufacture of other machine tools n.e.c.	29.43				
2477	Pigment manufacture	105.09.93	Manufacture of dyes and pigments	24.12				
2479	Characteristic processes in the manufacture of other non-metallic mineral products, involving fuel combustion; emissions from the glass production industry during manufacturing - Ni is used in coloured glass to give a green colour	104.11	Manufacture of flat glass	26.11; 26.12; 26.13; 26.14; 26.15	No ready replacement to use of Ni compounds as pigments			
2484	Paints manufacturing; emissions from paint and ink formulations due to use of Ni pigments	107.03.07	Manufacture of paints, varnishes and similar coatings, printing ink and mastics	24.30	No ready replacement to use of Ni compounds as pigments			

Nickel (continued)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
2487	Characteristic processes in the manufacture of pulp, paper and paper products, publishing and printing; emissions from the paper production industry due to the use of Ni pigments	105.07	Manufacture of pulp	21.11; 21.21;21.22; 21.23; 21.24; 21.25	No ready replacement to use of Ni compounds as pigments			
2494	Printing and dyeing operations	105.04.06	Preparation and spinning of cotton-type fibres	17.11;17.12; 17.13; 17.14;17.15; 17.16;17.17; 17.30; 17.51;17.52; 17.53; 17.54; 17.60; 17.71; 17.72; 18.10; 18.21; 18.22; 18.23; 18.24; 18.30	No ready replacement to use of Ni compounds as pigments			
2515	Batteries manufacturing	105.13.01	Manufacture of accumulators, primary cells and primary batteries	31.40	Important use in NiMH batteries which have replaced Cd and Pb based batteries			

Generic treatment options for Ni		B2 (addition of soda or caustic soda)	Wastewater treatment (BREF 02.03)	Discharge level 1 mg/l from feed of 50-250 mg/l or 1000 mg/l at pH 10); equivalent to 98 - 99.9% removal.
		B1 (using lime; dolomite; NaOH; soda) + A2 or A3 or A4 (sand) or A5	ditto	
		B10	ditto	80 - 99% removal for influent concentrations of 10-1ooo mg/l

3.20.   Nonylphenols (CAS No. 25154-52-3)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
1558	Characteristic processes in the manufacture of textiles and textile products	105.04	Manufacture of textiles	17	Alcohol ethoxylates and other ethoxylates are alternatives			
1559	Other industrial cleaning (except 107.02.0…..); use of detergent / cleaning agents / stain removers from outer-EU in industry (IPPC)	107.02.04	Manufacturing	D	Recommended replacements in detergents and cleaning agents are aliphatic alcohol ethoxylates which have increased biodegradability; need to consider toxicity which depends on alkyl chain length, chain branching and degree of ethoxylation			
1561	Characteristic processes in the manufacture of chemicals, chemical products and man-made fibres; emissions due to use in emission polymerisation and due to production of nonylphenols and nonylphenol ethoxylates	105.09	Manufacture of basic chemicals	24.0: 24.10				
1562_1	Characteristic processes in the manufacture of leather and leather products	105.05	Tanning and dressing of leather; manufacture of luggage, handbags and the like, saddlery and harness; manufacture of footwear	19.10; 19.20; 19.30	Substitutes are fatty alcohol ethoxylates and blends of these with aniionic surfactants.			
1565-3	Characteristic processes in the manufacture of pulp, paper and paper products, publishing and printing	105.07	Manufacture of pulp; manufacture of paper and paperboard	21.11; 21.12				

3.21. Pentabromodiphenylether (CAS No. 32534-81-9)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
1461_1	Polyurethane processing; release during production of flexible polyurethane foam for furniture/upholstery and automobile use, where flame retardant PBDE is added.	107.03.03	Manufacture of chairs and seats; manufacture of other office and shop furniture; manufacture of other kitchen furniture; manufacture of other furniture; manufacture of mattresses	36.11; 36.12; 36.13; 36.14; 36.15	Substitutes include metal hydroxides (e.g. Al and Mg hydroxide), organic and inorganic phosphates, phosphonates and phosphinates, melamine and melamine derivatives but none provide the same level of flame retardances at the same price and toxicity and ecotoxicity not well established.			

3.22. Pentachlorobenzene (CAS No. 608-93-5)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
2157	Pesticide production	105.09.95	Manufacture of pesticides and other agro-chemical products	24.20	Originally produced as a chemical intermediate for products which are now banned			
2163	Characteristic processes in the manufacture of chemicals, chemical products and man-made fibres	105.09				* B14 (steam or hot air) ** B14 + C3 *** flocculation + A2 + A4	Large volume organic chemicals (BREF 02.03)	* Discharge of < 1 mg/l of chlorinated organic compounds ** Discharge of combined penta - and hexa-chlorobenzenes of 1 ug/l *** for treatment of chlorinated organics adsorbed on particulates
			Generic treatment options for chlorinated benzenes			* B5 (495 °C for 3.6 minutes) ** B8 (NF) *** B12	Wastewater treatment (BREF 02.03)	* 99.99% removal of 1,2,4-trichlorobenzene ** 96% removal of trichlorbenzene *** Discharge of 10 mg/l from a feed of 100 mg/l representing 90% removal of chlorobenzene

3.23. Tributyltin compounds (CAS No. 688-73-3)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
2260	Characteristic processes in the manufacture of chemicals, chemical products and man-made fibres	105.09	Manufacture of other organic basic chemicals; manufacture of pesticides; manufacture of soap and detergents etc.,	24.14; 24.20; 24.50; 24.66				
2277	Paints manufacturing	107.03.07	Manufacture of paints, varnishes and similar coatings, printing ink and mastics	24.30				
2308	Production of plastic products (non-solvent processes)	105.10.11	Manufacture of plastic plates, sheets, tubes ; plastic packing goods; plastic builders ware; other plastic products	25.21; 25.22; 25.23; 25.24				
2316	Cleaning and washing without solvents	112.01	Preparation and spinning of clothing materials; leather treatment and manufactured goods; wood impregnation and wood products; finishing of textiles; production of electricity; building completion	17.11;18.22; 18.23;19.10; 19.20;19.30; 20.10; 20.20; 20.30; 20.40; 20.51; 17.12; 17.13; 17.14; 17.15; 17.30; 17.40; 18.10; 18.21; 40.11; 40.13; 45.40				
2340	Industrial laundries	111.04.02	Washing and dry-cleaning of textile and fur products	93.01				

Tributyltin compounds (continued)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
2347	Use of pesticides (other than agriculture and forestry)	107.06	Production of electricity; manufacture of pulp, paper; bee; rleather goods; textiles	40.11; 21.11; 21.12; 15.96; 18.10; 19.10; 17.11; 17.23; 17.24; 17.25; 17.30; 17.12; 17.13; 17.14; 17.15; 17.16; 17.17; 17.21; 17.22				
2471	Organometal manufacturing	105.09.94	Manufacture of other organic basic chemicals; manufacture of pesticides and other agrochemical products	24.14; 24.20	Substitutes for use as anti-fouling agent are copper, triazine compounds, silicone based poroducts, biological biocides, electrochemical methods and mechanical cleaning.			

| | | | Generic treatment options for tributytin compounds | | | A2 (using Al sulphate, ferric sulphate, ferric chloride, lime, polyAl chloride, polyAl sulphate or cationic organic polymers as coagulants) | Wastewater treatment (BREF 02.03) | > 90% removal |

3.24.   Trichloroethylene (CAS No. 79-01-6)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
2006	Pesticide production	105.09.95	Manufacture of pesticides and other agro-chemical products	24.20				
2007	Textile finishing	107.03.13	Finishing of textiles	17.30				
2008	Inks manufacturing	107.03.08	Manufacture of paints, varnishes and similar coatings, printing ink and mastics	24.30				
2009	Paints manufacturiing	107.03.07	Manufacture of paints, varnishes and similar coatings, printing ink and mastics	24.30				
2014	Dry cleaning	107.02.02	Washing and dry-cleaning of textile and fur products	93.01	Possible alternatives include perchloroethylene, methylene chloride and hydrofluorocarbons			
2020	Characteristic processes in the manufacture of textiles and textile products	104.04	Washing and dry-cleaning of textile and fur products	93.01				

Trichloroethylene (continued)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
2022	Chemical products manufacturing or processing	107.03	Finishing of textiles	17.30	Difficult to find a replacement feedstock without developing a new process			
2023	Printing industry	107.04.03	Manufacture of paints, varnishes and similar coatings, printing ink and mastics	24.30				

Generic treatment options for trichloroethylene		A2 (using Al sulphate, ferric sulphate, ferric chloride, lime, polyAl chloride, polyAl sulphate or cationic organic polymers as coagulants)	Wastewater treatment (BREF 02.03)	36% removal
		B14 (air) using spray aeration in a packed tower with an air/water ratio of 5/1	ditto	69-92% or 90% removal

3.25. Trifluralin (CAS No. 1582-09-8)

ES no.	Production process	NOSE-P class.	Production activity	NACE class.	Possibilities for substitution	Applicable treatment processes	BREF code of relevant document	Treatment efficiency and achievable emission levels
2170	Pesticide production	105.09.95	Manufacture of pesticides and other agro-chemical products	24.20	No longer authorised for use as a herbicide in the EU			
			Generic treatment options for trifluralin			B8 (RO)	Wastewater treatment (BREF 02.03)	99% removal