

Water treatment

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1 Outline of the topic of water treatment

1.1 Links to physics, chemistry, biology

The preparation, treatment or purification of water plays an important role in very many aspects of our lives: preparation of drinking water for private households, preparation of non-potable and process water in industry, treatment or purification of water in recirculation processes such as for swimming pools or in many industrial production processes, treatment of waste water. The processes applied are divided into physical, physical-mechanical, physical-chemical, chemical and biological processes. They are in principle the same in all areas of application, even though they are applied on differing scales and refinements in practice.

This guideline therefore presents the processes in their scientific-technological context. In the spirit of applied rather than abstract lessons, the "elixir of life" helps to establish entry points to scientific subjects.

1.2 Treatment, purification, preparation – clarification of terms

The terms are used differently in the strict terminology of the various fields. Strictly speaking, "treatment" is the comprehensive generic term. In practice in the various fields, it is always used when a change in water quality is referred to. Sometimes "neutral" sounding usage is necessary, so that treatment is still the preferred word where there is a high or even dangerous level of pollutants. Thus waste water disposal experts sometimes talk about treatment, sometimes cleaning or purification of the waste water and always mean the same thing.

In the preparation of drinking or pure water on the other hand, "preparation" is used where the quality of the water found is insufficient for the intended purpose. Hence preparation of raw water (well water, spring water, ground water etc.) to drinking water or preparation of drinking water to ultra-pure water in the pharmaceutical industry etc.

2 Physical processes

2.1 Mechanical separation by particle size

2.1.1 Screens or sieves

For the separation of relatively coarse solids with hole or mesh sizes of approx. 0.5 to 10 mm the term sieve is used, for sizes of 10 cm and more the term screen. They are used, for example, during the extraction of raw water for industrial and drinking water from rivers and lakes, and also in the initial stage of sewage plants.

2.1.2 Filtration

Filtration means the separation of solids from liquids through the pores of a filter medium that solids beyond a certain size cannot pass through. These separation barriers can be the pores of paper or plastic membranes, but also the pores in minerals themselves (kieselguhr, aluminum oxide) or the fine spaces between compact grains of sand ("filter bed"). In addition to separation due to particle size (sieve effect), adhesion of small particles to the surface of the filter grains plays an important role in particle separation as part of drinking water treatment. The pore sizes can be so

small that they are the size of molecules (nanofiltration).

Sand filters

Sand filters are frequently used to remove suspended solids from the water. The term suspended solids is used if the solids distributed in the water ("suspension") are particularly fine and relatively light. In other words, separation through sedimentation would take a very long time. The filter comprises a layer made of quartz sand grains of various sizes. The suspended solids are filtered out and held back in the pore cavities between the quartz sand grains; this increases the filter resistance the longer the filter is used. Sand filters have to be regularly flushed out to protect them against complete blockage. This is done using pure water, and if required with an air-water mixture, in the opposite direction. The waste water from this flushing operation also has to be cleaned. Sand filters are standard filters in the first stage of turning raw water into drinking water or process water in industry and also in the final cleaning stage of sewage plants.

Paper filters

Flat paper filters as used in chemical labs or familiar from chemistry lessons, but also paper filter cartridges and suchlike are not used for water treatment as a rule. For these filters are disposable filters and the material and labor costs (replacement) would be too high when treating large quantities of water.

Membrane filters

Nowadays plastic membranes are used, even though in principle metal and ceramic membranes are also possible. Depending on the size of the particles to be separated, the terms microfiltration, ultrafiltration, nanofiltration and reverse osmosis are used.

Microfiltration	These filters are mostly made of organic material or ceramic and have a pore size in the micrometer range from 0.05 to 10 µm. Finely suspended solids, such as fibers, proteins and larger microorganisms (amoebas), can be filtered out with them. There must be a hydrostatic pressure difference of approx. 0.1 to 2 bar to overcome the membrane resistance. They are used, for example, to remove fine paper fibers from the recirculation water in paper mills or for post-treatment of purified wastewater.
Ultrafiltration	Ultrafiltration is used with pore sizes of about 0.005 - 0.015 µm. This can filter out macromolecules, viruses, colloids and bacteria. The pressure difference must be about 0.1 to 5 bar. This type of filtration is used, for example, as the main stage or pretreatment in the preparation of pure and ultra-pure water in the food and beverage, pharmaceutical and semiconductor industries. In drinking water treatment, ultrafiltration membranes may be used to remove particulates, in order to ensure the success of subsequent disinfection.
Nanofiltration	Nanofilters, mainly made of homogeneous polymer layers, are used with pore sizes in the nanometer range from about 0.7 to 10 nm. These can filter out organic compounds, ions (bivalent), dyes, pesticides, and also herbicides. They require a pressure

	<p>difference of 3 to 20 bar and even then the pure water throughput is only 10 to 15% of that in a microfilter. This is an important stage in the preparation of ultra-pure water, and also in the pre-treatment stage for waste water from certain contaminating production processes.</p> <p>Ultra- and nano-filtration as a physical-chemical process: Strictly speaking, a membrane filter with the smallest pore size no longer functions as a mechanical filter. If the pore size is similar to the size of the molecules or ions to be allowed through or to be blocked, the adhesion forces between the particles and the edges of the pores also play a role. The molecular form of the substances to be filtered and the type of the chemical binding forces both in the membrane itself and also in the substance to be filtered play an important role. Hence molecules or ions that are smaller than the membrane pores are in many cases held back nevertheless.</p>
Reverse osmosis (RO)	<p>The principle: In line with the natural law of dispersion, all substances, be they gas molecules, metal atoms or ions in solutions, continue to disperse "on their own" until the same concentration is achieved throughout. When two solutions are brought into contact via a boundary (for example a permeable membrane), matter is "automatically" transferred until an equilibrium is achieved. Semi-permeable membranes, however, only allow certain substances, for example water molecules, to pass through the membrane pores. In this case, equilibrium of all the substances cannot be achieved in the system as a whole. For example, when pure water is brought into contact with concentrated sugar solution via a membrane permeable only for water (classroom experiment), water continues to flow to the sugar solution until the hydrostatic pressure (rise in the liquid height) on the sugar side is so high that the transfer stops. The Greek word for "transfer" is "omosis". The process in physical chemistry is known as "osmosis" and the limiting pressure as "osmotic pressure". Because of osmosis, cells in the human body absorb salts and sugar from the blood or sap "shoots" in plants in the spring. Increasing the pressure on the sugar solution side above the osmotic pressure forces the water back to the pure water side. This is called reverse osmosis.</p> <p>Areas of use: Reverse osmosis can separate out the smallest particles such as molecules and ions. Reverse osmosis is used for particle diameters in the range of less than approx. 1 nm. It can be used to separate out alkali and alkaline earth salts, but also heavy metal ions and alcohols and sugar. Typical pressures are approx. 10 to 100 bar. The best known area of use is probably the desalination of sea water to produce drinking and process water. Reverse osmosis has become one stage in the standard procedure for the "detoxification" of waste electroplating process water or in the producing of ultra-pure water.</p>

Counterflow filtration

In every type of filter, the pores block up sooner or later, the filter resistance becomes so large that the filter process, i.e. the separation process, comes to a halt. As explained for sand filters, the filter can be flushed clean in the opposite direction in intervals or even automatically. This is also possible in principle for fine membrane filters, but it requires relatively high pressures. In addition, the downtime and maintenance both cost money, therefore uninterrupted processes are preferred in industry. This is possible if the liquid flow to be filtered and the filtrate flow are parallel rather than vertical to the membrane. In optimized processes, the filter membrane continuously flushes itself clean. In ultrafiltration for drinking water treatment, counterflow filtration (or cross-flow filtration) is the exception. Here, all of the water that comes to the membrane actually gets through. This is called dead-end filtration, since by comparison with counterflow filtration it requires the water to have a lower turbidity load, but also requires considerably less energy.

2.2 Mechanical separation by density

2.2.1 Sedimentation

Sedimentation is the term used when finely distributed solids in the water, i.e. suspended substances, settle on their own due to gravity. This means that the sedimented substance is heavier or has a higher density than the liquid. Sand traps, grease traps and primary settlement tanks in sewage plants are good examples in water treatment. The importance of sedimentation as a natural process can be seen from the fact that many soil layers, such as shale and shell limestone, are the result of long periods of sedimentation.

2.2.2 Hydrocyclones

In the laboratory, centrifuges are used to accelerate the deposition of suspended substances. This technology is of course not feasible for large quantities of water. In process engineering cyclones are used instead. Just as air can be made to rotate in modern bagless vacuum cleaners, water can be made to rotate when channeled appropriately. Heavy particles tend to collect on the outer edge where they can be continuously removed. This process is used where there is a particularly high level of relatively heavy suspended solids both in waste water treatment and also raw water treatment.

2.2.3 Flotation

Flotation is used to remove relatively light substances from suspensions as quickly and efficiently as possible. Air is injected from the bottom into the water flowing at a right angle to gravity (parallel to the floor). The air bubbles at the water-air boundary collect the relatively light suspended solids and raise them to the surface where they are continuously removed. This process is used where there is a particularly high level of relatively light suspended solids both in waste water treatment (primary settlement tank, secondary stage 2) and also raw water treatment. Flotation is also used in the plastics and paper industry to remove droplets, pellets and fibers from the recirculation water.

2.3 Thermal separation by boiling point

2.3.1 Distillation – the principle

Mixtures of liquids can be separated because of their different boiling points, as every distiller knows. But there is not 100% separation in each distillation cycle (distribution equilibrium). Therefore repeated or multistage distillation is required. If the liquid contains dissolved salts and solids, these remain after the solvent has been evaporated. In this case, 100% separation is possible.

2.3.2 Distillation for desalination

Distillation is the standard process for producing raw water from sea or brackish water to make drinking and process water. The traditional processes consume so much energy, however, that reverse osmosis is increasingly being used. Modern processes, however, use the sea water to be distilled as cooling water, so that almost 100% of the condensation heat can be recovered. In counterflow distillation plants with up to 16 stages, the energy consumption can be reduced to approx. 15% of that in traditional plants. This explains why thermal desalination plants are experiencing a renaissance particularly in Arab countries, because they can put the natural gas from the oil fields that would otherwise simply be flared off to good use and spare the environment at the same time.

2.3.3 Distillation for producing ultra-pure water

Only 30 years ago "aqua bidestillata" was still the standard for ultra-pure water in medicine and the pharmaceutical industry. Nowadays, distillation is mostly used only as the final stage – for example after desalination, deionization and ultrafiltration – in the production of ultra-pure water.

3 Physical-chemical processes

Strictly speaking, these also include **nanofiltration** and **reverse osmosis**, which were discussed above.

3.1 Gravity and chemistry

3.1.1 Problem case: separation of colloids

Where substances are present as minute particles smaller than a micrometer, they settle extremely slowly even in a large density. They do not agglomerate because they tend to have a negative electrical charge which keeps them "at bay". Such "suspensions" are called colloids. Theoretically, they can of course be separated using ultra- and nano-filtration, but this is far too expensive for large quantities of water. Here "flocculation" is used to aggregate the finest particles to larger particles, which then sediment in a reasonable amount of time.

3.1.2 Flocculation

First of all cations (multivalent positive ions, mostly ferrous and aluminum salts) are added to this flocculation. These discharge the negative colloid particles, which form larger positively charged

agglomerations ("flocules"). If lime or sodium hydroxide solution is now added, alkaline hydroxides precipitate out that attach to the flocules and are deposited out with them.

The efficacy of flocculants can be boosted with modern flocculation aids. The flocculation aids that promote networking of individual flocules are synthetic polyelectrolytes (multiply-charged positive or negative water-soluble polymers, for example acrylates). In industry, flocculants are mostly used to treat waste water from mining or refineries as they accelerate the settlement or filtration processes.

In the case of problematic raw water (such as river water), flocculation is frequently used in the first stages in the production of drinking, non-potable and process water.

In waste water treatment, flocculation is also used in preliminary and secondary settlement. An additional effect of flocculation is that low traces of heavy metal ions or various non-readily degradable organic compounds are "embraced" by the flocules and so precipitated out as well.

3.2 Membrane filtration in an electrical field

3.2.1 Electro-deionization – the principle

Electro-deionization basically functions on the same principle as reverse osmosis. Two aqueous solutions with electrodes in them are brought into contact via a semipermeable membrane. Applying a positive or negative voltage causes the cations or the anions to pass through the membrane. Unlike in reverse osmosis, it is not the water but the salt ions that move and the driving force is not pressure but an electric field. Regeneration is not necessary. This makes it an extremely environmentally friendly process.

3.2.2 Electro-deionization for removal of certain ions

The pore size and voltage can be varied to remove particular sorts of ions. If necessary, to almost a 100% extent (see next section). Electro-deionization is nowadays used, for example, to remove hazardous heavy metal ions from process waste water.

3.2.3 Electro-deionization for demineralization in ultra-pure water production

In reverse osmosis, the mechanical limits of the membranes and the expense of building the plant to withstand the pressure tend to restrict the applicable pressure and pore sizes so that at most 99.3% desalinated water is possible in practice. Electro-deionization on the other hand causes no such construction problems. Continuous fresh water flushing (with drinking water) on the salt separation side of the membrane can shift the distribution equilibrium extremely in the favor of separation. It depends only on the throughput speed and the volume of flushing water whether desalinated water of 99.99% or more is achieved. In ultra-pure water treatment, for example for the semiconductor production (chips), "rough desalination" using reverse osmosis is now followed by electro-deionization for genuine demineralization or deionization.

3.3 Adsorption

3.3.1 Surface binding as borderline case of chemical binding

The adsorption of gas molecules or dissolved molecules on the surface of solids is a borderline case between solid-state physics and chemistry. Traditionally the effect is considered part of phys-

ical chemistry, but nowadays of surface science (physics and chemistry of surfaces). Strictly speaking, adsorption arises when binding forces between the molecule and solid body are greater than the pure Van-der-Waals forces. That a bond arises at all, for example, between a herbicide molecule dissolved in water and the surface of a carbon crystal, is due to the presence of broken bonds on the absolute boundary of solids. A chemistry teacher would say: a carbon atom on the surface is held by three of its four possible bonds, the fourth valence protrudes. In graphite, the relatively weak fourth bond protrudes, thus offering energetically favorable docking to a wide range of different types of molecules. Certain minerals like bentonite, zeolite and aluminum oxide are particularly suitable as adsorption filters.

3.3.2 Adsorption by activated carbon, a standard procedure in chemistry

Owing to this special surface characteristic of carbon, graphitic carbon with its especially large surface has been in use as an adsorption medium for over 100 years now. The large surface is due to the porous structure achieved by converting wood into "activated carbon" by dry distillation and treatment with steam and water. Nowadays, specially treated hard coal (anthracite filter) and lignite are used on a large scale as "activated carbon".

3.3.3 Activated carbon filters in water treatment

In water treatment, raw water contaminated with herbicides, pesticides, fungicides, oils, medicines, chlorinated hydrocarbons, aromates and other hydrocarbons is cleaned by activated carbon filtering. Depending on the contamination and the statutory requirements, the "used" filter material loaded with the adsorbed substances has to be disposed of in expensive special waste incinerators dumps or incinerated in coal-fired power plants. But it can also be regenerated in special plants. Activated carbon filters are technologically simple and efficient, but ultimately relatively expensive and environmentally unfriendly to disposal of.

Activated carbon filtering is used to counter particular types of contamination in the **raw water treatment for drinking and process water**. In the case of contamination that affects microbial degradation in the biological stage of the sewage treatment, activated carbon is used in the preliminary settlement of the **waste water**. When the treated water has to meet special quality requirements, for example, if it is going to be discharged in waters used for swimming or into ground water for the production of drinking water, activated carbon is also used for secondary settlement in waste water treatment.

In the pretreatment of **industrial waste water** from particularly contaminated production processes, activated carbon is still the standard procedure but is increasingly being replaced by "waste-free" processes (such as membrane filtration, oxidative or chemical degradation with peroxides, ozone, UV).

4 Chemical processes

4.1 Ion exchange

Salts solubility depends on the bonding energy of the salt ions to each other, and on the hydration energy of the salt ions in water. If the hydration energy of the salt ions is higher than their mutual bonding energy, the ions will dissolve in water. This also applies when these salts are bound not to each other, but to the surface of minerals (certain zeolites) or artificial resins. If, for example, such a surface has sodium or hydrogen ions, these can dissolve in water on contact if other ions present

in the water, such as calcium ions, take their place on the surface, hence the name "ion exchanger". If the water solubility of the sodium or hydrogen on the ion exchanger is greater than that of calcium, the exchange will continue until a distribution equilibrium is reached (see Nernst law of distribution).

4.1.1 Softening

"Normal" water softening in domestic systems, but also in the drinks industry, is achieved using ion exchanger systems. The hardeners Mg^{2+} or Ca^{2+} are replaced with Na^+ . Once the exchange process is exhausted, the ion exchanger is regenerated with sodium chloride (NaCl). This is the case in dishwashers, for example.

4.1.2 Deionization – demineralization

All the cations dissolved in the water, for example also those of heavy metals, can be removed through "complete" replacement with H^+ -ions. The ion exchanger is then regenerated with acids (such as hydrochloric acid). This is often wrongly referred to as demineralization or deionization. Strictly speaking, for demineralization not only the cations but also all the anions (chloride, sulfate etc.) must be removed from the water. This is possible with additional anion exchangers. In special cases, ion exchange is used for deionization during the pretreatment of heavily contaminated process waste water in industry. Where process water preparation has to meet high purity requirements, other fully continuous processes without chemical regeneration are used (see also Electrodeionization).

4.2 Adjusting the pH value

4.2.1 pH value – the power of hydrogen

The "Puissance Hydrogène" is the negative logarithmic measure for the concentration of hydrogen ions. The pH value states whether an aqueous solution – based on the neutral level – has an excess or deficit of hydrogen ions (H^+ = "protons"). A pH value of 7 means the solution is neutral. A pH value under 7 means the solution is acidic. A pH value over 7 means the solution is alkali. Depending on the pH value, certain – in part desirable, in part undesirable – chemical or biochemical reactions are expedited or slowed down.

4.2.2 Neutralization

In the drinking water network, acidic water quickly leads to corrosion, too chalky water to scale. This shortens the useful lives of the pipes and their premature, expensive replacement. Therefore, neutralization is of **key importance in drinking water preparation**.

During **drinking water preparation**, an excessively low (acidic) pH value is adjusted to pH values by removing carbon dioxide dissolved in the water (carbonic acid) or filtering it through limestone (marble chips or partially-burned dolomite). The lime dissolved in the water and the remaining dissolved carbonic acid are then in equilibrium (lime-carbonic acid equilibrium). Depending on the hardness of the water, this equilibrium pH can be between 6.5 and 7.5.

During **waste water treatment**, the pH value of the waste water in the preliminary settlement is often adjusted to neutral to slightly alkaline using lime. This supports phosphate precipitation with

ferrous salts and reduces the solubility of heavy metals which then also precipitate out. A too low or acidic pH value would also slow down the aerobic degradation in the biological stage.

For ultra-pure water for processes in chemistry, the pharmaceutical industry and chip production, a sodium hydroxide solution (before desalination or deionization) is used to adjust the pH value to as close to 7 neutral as possible.

4.2.3 Acidification

Acidification is used during sludge treatment in a **sewage plant** for generation of biogas in the digestion tower. The biochemical digestion reactions run excellently in an acidic environment.

4.3 Chemical degradation and conversion

4.3.1 Photolytic degradation with UV light

High-energy radiation can excite the chemical bonds in otherwise non-readily degradable substances so strongly that they break up. The molecules break down into simpler, as a rule easily degradable substances.

4.3.2 Water disinfection with UV light

The fact that practically all microbes – be they bacteria, viruses, fungi etc. – die or cannot reproduce when exposed to high-energy UV light is also due to photolysis. Only here as a rule it is the chemical bonds in the DNA that are broken.

Since this highly effective process neither requires chemical regeneration nor has any waste products, it has become one of the standard procedures for the preparation of **drinking, non-potable and process water**. Even in the production of ultra-pure water for the pharmaceutical industry, it is often used as an additional disinfection stage along with other processes such as ultra- and nano-membrane filtration. (Killing microbes with UV light, separation of the dead organisms and endotoxins by filtration).

4.3.3 UV light against legionellas in the home, hotels and swimming pools

Where water stands in tanks and pipes over longer periods of time at temperatures above approx. 25 °C, legionellas, which cause pneumonia, can breed very quickly. Only constant water temperatures of well under 20 °C or over 60 °C are a reliable protection. UV treatment systems integrated in the water pipes can reliably kill these legionellas.

4.3.4 Oxidation

Oxidation is the term used for all reactions with substances that can take up electrons. This includes oxygen, ozone, chlorine and permanganate. Examples of such reactions are the combustion of hydrocarbons (petrol, diesel, natural gas) into carbon dioxide and water, or the oxidization of pesticides in untreated water by ozone. During water treatment, these processes occur not as rapid combustion but as slow oxidation.

4.3.5 Oxidative pollutant degradation with atmospheric oxygen

This is a standard process involving aerobic microbes in the biological stage of the **sewage plant**. In drinking water treatment, it is sometimes used as a special case in fixed bed bioreactors. Even when oxidative biological processes are not used intentionally, they take place in almost all filters used to separate out particles.

4.3.6 Oxidative pollutant degradation and disinfection with peroxides and ozone

When ozone (O_3) or peroxides break down they release atomic oxygen as oxygen radicals. Whilst molecular oxygen requires higher temperatures (activation energy), oxygen radicals oxidize many pollutants even at low temperatures. Perborates, percarbonates and particular persulfates work especially quickly, thus enabling shorter treatment times. But they leave salt solutions and not pure water. Better for the disinfection of pure water are hydrogen peroxide (H_2O_2) and ozone, because they break down without any residues. They are used in chemical-oxidative processes also in combination with UV light.

4.3.7 Combination of oxidative and photolytic processes

If the water contains organic compounds that are extremely hard to break down, peroxides and ozone often in combination with UV light are used in the production of ultra-pure water, but also in the pretreatment of process waste water. This guarantees reliable degradation in relatively short treatment times.

4.3.8 Chlorine for disinfection

Ultimately, treatment with chlorine gas, chlorine dioxide or sodium hypochlorite is an oxidation process: chlorine and water break down via the hypochlorite stage to hydrochloric acid and atomic oxygen. Even though the hypochlorite alone damages many microbes, the atomic oxygen is just as effective. Since the treatment changes the pH value or leaves sodium and chlorine ions as a residue in the water, "chlorination" is no longer used for producing process water as a rule. It remains a standard procedure, however, in **drinking water treatment and in swimming pools**. The dissolved chlorine or hypochlorite has a relatively long life and so ensures even and lasting disinfection even in widely dispersed systems.

4.4 Separation by solubility

4.4.1 Solution equilibrium permits precipitation

Depending on the temperature, there is a certain percentage of undissolved substance in equilibrium with the dissolved in every water-soluble ionic compound ("salt"). The undissolved part can thus be separated by sedimentation or filtration. Many salts, however, are so soluble that this is not a feasible approach.

Often the oxidation stage of the ions determines how high the solubility is. For example, bivalent iron and manganese dissolve well in water but not the trivalent forms.

Adding a solution of a different dissolved salt to a solution of a "completely" dissolved salt can cause the anions and cations to combine in a different way. For example, the cations of salt A and the anions of B form a salt with low solubility which precipitates out and so can be removed.

4.4.2 Deferrization and demanganization of drinking water

Non-soluble oxides and hydroxide are formed if the iron and manganese ions in the raw water are oxidized by means of intensive aeration by flowing over cascades or injecting atmospheric oxygen into the raw water. These precipitate as floccules and can be removed by a sand filter. However, a higher quality of drinking water is obtained when the water is only weakly aerated and the oxidation process itself is done by microorganisms in a sand filter. The oxides and hydroxides thus produced adhere more firmly to the filter grain than do floccules separated in the filter.

4.4.3 Precipitation of phosphate from waste water with ferrous salts

Iron and aluminum phosphate are not very soluble in water, therefore phosphate in the waste water can be precipitated out by adding readily soluble iron and aluminum salts. These examples also clearly show that the solubility can also depend on the pH value. In acidic water the iron phosphate would remain dissolved, in slightly alkaline water solubility falls but increases again in the strongly alkaline range. So slightly alkaline calcium carbonate is added during dephosphorization to raise the pH value to approx. 7.2.

5 Biological processes

These processes work with the indirect use of chemical processes via the metabolic and reproduction processes of microbes such as bacteria, protozoa, fungi. This involves biochemical processes. These processes are described in detail in the guidelines on waste water and drinking water.