

Water Purification: Physical, Mechanical, Chemical and Biological Treatments

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ABSTRACT

Water purification is a physic-chemical and biological process that consists of the removal of contaminants from raw water, through the use of different technologies (mechanical, physical, chemical, biological), to obtain water suitable for normal domestic consumption, for irrigation of fields or for industrial uses. The uses of water are the following: drinking, agricultural, for swimming pools, industrial processes (cooling, steam production and fire-fighting systems).

Keywords: Waster Water, Water Treatment Plants, Pollutants, Filtration, Ion Exchange, Disinfection, Clarification.

INTRODUCTION

Water pollution is not only responsible for 25 different types of diseases, but also for the reduction of biodiversity and the destruction of many aquatic species. Chemistry, with the entire life cycle of its products, is one of the responsible for this pollution, but it is also the sector that in the last twenty years has given a great contribution, with continuous efforts, in the research to make water clean and hygienically pure [1-19]. The uses of water are the following: drinking, agricultural, for swimming pools, industrial (process, cooling, steam production and fire-fighting systems). Purified industrial water can have the following reuses: for process water, for heating, for cooling, for fire-fighting services, discharge into surface water and discharge into the consortium sewer system. Water pollutants are: dissolved and suspended inorganic substances; large organic and inorganic materials (plastic, paper, sand and oils), pathogenic substances, turbidity, mineral oils, suspended and settleable materials, metals, dissolved non-biodegradable and biodegradable organic substances (dyes, surfactants, phenol, pesticides, solvents and dyes, sulphides, volatile organic compounds, fats, chlorinated substances), toxic organic and inorganic substances and fertilizers nutrients N and P.

The purification treatments of primary and waste water are the following: mechanical, physical, chemical, biological and disinfection which are part

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of the physical and chemical treatments. The mechanical treatments are: screening, oil removal, sand removal. The physical treatments are: flotation, evaporation, sedimentation, mechanical filtration, separation with membranes, physical adsorption, disinfection (UV). The chemical treatments are: coagulation, flocculation, precipitation, chemical adsorption, ion exchange, oxidation-reduction, neutralization and disinfection. The biological treatments are: aerobic or anaerobic (oxidation, nitrification and denitrification). These treatments take place in the following successive time phases: preliminary treatments (screening, sand removal, oil removal); primary and also tertiary treatments: oxidation, reduction, precipitation, clari-flocculation, neutralization, filtration, flotation, use of membranes and ion exchange; secondary treatments (biological processes and sludge sedimentation); tertiary treatments only (physical adsorption and disinfection). Water treatment is one of the most complex technologies in the chemical industry and this is due to the following reasons: individual pollutants require different treatment technologies; for each individual pollutant there are different alternative treatment technologies; the technologies to be chosen for each individual pollutant depend on the presence of other pollutants, on their concentration, the quantity of water to be treated and the type of use of the water; there are energy costs, management costs (sludge disposal costs), environmental costs (greenhouse gas emissions CO₂, NO_x, CH₄), the costs of disposing of sludge as waste and the costs of chemical reagents.

MECHANICAL AND PHYSICAL PURIFICATION

In this paragraph are reported the mechanical treatments and the following physical technologies for purification of water: flotation, sedimentation, mechanical filtration, quartzite and active carbon filter, physical adsorption, membrane processes, disinfection UV reported in references more general [1-19] and in references [20-35] related to this paragraph.

MECHANICAL TREATMENTS

Mechanical treatments, which are carried out in the preliminary purification phase, are: the elimination of suspended solid or liquid substances that can negatively influence subsequent purification treatments and consist of the following phases [1-21]: screening, i.e. the separation of coarse non-sedimentable solids (rags, plastic, etc.); sand removal, i.e. the separation of sedimentable suspended solids (sand and soil); oil removal, i.e. the separation of oily substances. Coarse

screening separates large solids by passing the water through a grid that blocks the suspended solids and retains materials larger than 2÷5 centimetres (wood, rags, various materials) carried by the waste water; the grid consists of a steel frame with bars placed vertically and spaced 2÷5 cm apart. Fine screening serves to retain suspended particles larger than 1÷1.5 millimetres and is performed with machines called rotary sieves. The retained material is sent to a compactor by means of a screw and bagged in special "big bags". The sand traps consist of reinforced concrete tanks through which the sewage and coarse sedimentable solids (gravel) pass at a speed that causes the solid materials entrained in suspension to settle. The de-oiling of water consists in the elimination of oily substances, characterised by a lower specific weight than that of water, and which rise and remain on the surface by floating. The removal of oily and greasy substances is carried out periodically by means of a system that scrapes the surface of the wastewater.

PHYSICAL TREATMENT

For all physical treatments reported in this paragraph there are general information in references [1-19] and specific information in references [22-34].

FLOTATION

Flotation is located downstream of clariflocculation (a chemical treatment carried out in the primary and tertiary sectors that produces larger solids). Flotation consists in the separation and collection of material on the surface of a liquid [22-24]. This separation is obtained with very small air or gas bubbles that incorporate the particles to be eliminated and bring them to the surface. With the help of dissolved air flotation, the problem of the poor sedimentability of the flocs is overcome. The bubbles generally have a diameter between 50 and 80 microns and attach themselves directly to the flocs, modifying their specific gravity, with a prompt rise to the surface. In flotation, air at 4.5 atm is used and very fine air bubbles are formed, which slowly rise upwards, dragging with them the suspended flakes obtained in clari-flocculation. Air and solids collect on the surface in the form of dense foam, which is then collected by a scraper.

SEDIMENTATION

Sedimentation (also called clarification) is the last stage of clariflocculation and is also located downstream of the biological treatment to eliminate the activated sludge [25,26].

This treatment is based on the principle of precipitation in the tanks where the suspended solids settle. The tanks are a maximum of 180 cm deep to prevent weather conditions from causing the water to mix; the tanks are sized to ensure a residence time of the sewage between 1 and 3 hours.

MECHANICAL FILTRATION

Filtration is localized: 1) after the primary sedimentation downstream of the clariflocculation, 2) after the secondary sedimentation downstream of the biological treatment and 3) downstream of an oxidative treatment to eliminate iron and manganese. Once the coarser suspended particles have been eliminated, the water can go to the filtration process. In this paragraph we will only talk about mechanical filtration [27-29], which consists in the elimination of suspended solids, colloids and turbidity, with quartzite and anthracite and in the elimination of organic substances on active carbon. There are other types of non-physical filtration such as: biological filtration (with ferments adsorbed on the filter), ion exchange filtration, membrane filtration (reverse osmosis, nanofiltration, ultrafiltration and microfiltration), catalytic filtration to transform soluble substances based on Fe^{2+} and Mn^{2+} into solids, filtration by chemical adsorption (elimination of As and Se) and sludge filtration. In mechanical filtration, suspended solids, colloids and turbidity that remain in the pores and on the surface of the filter media are eliminated. The filters are based on quartzite, anthracite, quartz sand, anthracite followed by quartzite and quartz sand filters, quartzite followed by active carbon filters.

QUARTZITE AND ACTIVATED CARBON FILTERS

Quartzite is quartz ground to 98% silica, quartz sand is made up of 85% silica, anthracite is 90% carbon (to eliminate algae and sources of turbidity). Mechanical filtration removes any particles of sedimentable or suspended material that escaped previous treatments from the water, in particular it is used to eliminate suspended solids [30,31]. Filtration can also be used as a final treatment for drinking water and primary water (with sand and carbon). In technical literature, the word activated carbon is used not only in filtration but also in physical adsorption. Filters work by making the water pass through the filter following a flow from top to bottom, cleaning the water of debris, progressively retained by the pores. However, over time, this debris tends to become an obstacle to the passage of water, thus making the filtration process less

effective. Periodically, a backwashing operation of the filter is in fact necessary. Mechanical filters based on quartz sand, quartzite and anthracite are purified by backwashing, using air + water flows directed upwards, to fluidify the filter bed, separating the granules from each other and promoting the removal of the retained suspended solids. Backwashing is essential for the correct functioning of the filter and represents approximately half of the entire cost of the plant. Quartzite or quartz sand filtration is used to eliminate solids, while quartzite and anthracite or anthracite-only filtration is used to eliminate solids and turbidity and organic substances. The exceptional filtering action of anthracite is due to the irregular shape of the grains that form intergranular voids, allowing high filtration speeds with low pressure losses and allowing high quantities of impurities to settle. The overlapping of different anthracite layers with different grain sizes allows solids that can be of different sizes to be retained on each of the different layers. Quartzite or quartz sand filters are made from filtering material with differentiated grain sizes, placing the smaller grain size in the upper part of the bed; furthermore, to further improve the filtration capacity, a top layer of anthracite can be inserted which removes the larger particles by introducing 20% anthracite and 80% quartzite. In quartzite and activated carbon filters, the first filtration is on quartzite (or sand) and anthracite which remove from the water any particles of sedimentable or suspended material that escaped the previous treatments. The second filtration is by adsorption on active carbon which eliminates residual organic substances, such as hydrocarbons, non-biodegradable organic substances and also phosphates and inorganic ions.

PHYSICAL ADSORPTION

Physical adsorption is generally the first tertiary treatment after the biological treatment [32]. Physical adsorption is carried out on active carbon (they use the word activated carbon) of non-ionic organic substances, but soluble in water and their subsequent removal. There are, however, other types of adsorption that are not physical and are the following: there is an electrostatic adsorption called ion exchange; there is a chemical adsorption by interaction with hydroxides called clariflocculation; there is a chemical adsorption on alumina and on zeolites. Activated carbon is practically the only physical adsorbent used and is pure carbon obtained from fossils or natural substances with a surface area of 500-1,500 m^2/g (i.e. very porous) and is used: 1) as granular

activated carbon (Gac) (0.4-2.5 mm) in adsorption columns downstream of a biological treatment; 2) as granular activated carbon (GAC), together with quartzite as a decolorizing filter and to eliminate organic substances; 3) as powdered activated carbon (PAC) dispersed in aqueous solution under stirring and then subjected to sedimentation (not reactivatable). The adsorption process occurs in the following phases: macro-transport i.e. movement of organic material through the macro-pore system of the activated carbon (pores >50 nm); micro-transport or movement of organic material through the micro-pore system. Activated carbon adsorption is used for the following purification processes: to eliminate toxic compounds; to lower the chemical oxygen demand (C.O.D., non-biodegradable organic substances); to reduce colors and odors; to avoid the formation of foam; to promote the conditioning of sludge in biological treatment plants; in dechlorination and deozonation treatments; in the filtration of swimming pool and aquarium water. The presence of turbidity or suspended solids in the water to be treated reduces the carbon adsorption capacity, as it causes a partial occlusion of the porous structure, reducing the surface available for adsorption. It is necessary to send previously clarified and, if necessary, filtered waste water to the activated carbon treatment. Powdered carbon is eliminated with the sludge, while granular carbon is regenerated. Spent carbon can be regenerated using the following techniques: solvent washing, acid or alkaline washing, steam regeneration and thermal regeneration. The almost universally adopted technique is thermal regeneration, carried out at a temperature of 900-930 °C, in a low oxygen atmosphere. In these conditions, the organic substances are completely burned or vaporized, with minimal carbon combustion (10% is lost). The advantages of physical adsorption on active carbon are that it allows the removal of compounds that are refractory to biological treatment and also the recovery of organic compounds, while the disadvantage is the energy costs in regeneration.

MEMBRANE PROCESSES

Physical membrane processes are located in both the primary and tertiary sectors and are alternatives to other physical and chemical treatments [33]. Membrane filtration is an alternative to flocculation, adsorption (sand filters and activated carbon filters), and exchangers, solvent extraction and distillation. Membrane purification processes are used to remove suspended solids, colloids, emulsion oils, bacteria and

dissolved salts. The membrane filtration process (also called membrane cross-flow filtration) consists of separating water into two flows, permeated water and concentrated aqueous solution (which contains suspended particles or concentrated salts). A membrane constitutes a physical barrier that allows one or more species to pass and prevents and slows down that of others.

The choice of installing one or more types of membrane depends on: the quality of the fluid to be filtered, the chemical composition of the incoming fluid and the quality of the water you want to obtain. The types of purification with membranes are the following: microfiltration (MF), i.e. separation of colloids, suspended solids, microorganisms, and requires very low pressures and <2 bar and separates based on the size of the substances to be eliminated; ultrafiltration (UF), i.e. separation of macromolecules with different molecular weight and requires low pressures <10 bar and separates based on the size of the substances to be eliminated; nanofiltration (NF) i.e. separation of molecules, sugars, salts and requires high pressure <20 bar and separates based on the size but also on the chemical affinity of the substances with the membranes; reverse osmosis (RO) i.e. separation of ions and requires high pressure up to 100 bar and separates based on the size and chemical affinity of the chemical substances with the membranes. There are other membrane processes that are not only physical such as: MBR membrane reactors with biological purification and simultaneous separation of activated sludge; dialysis (D) and electrodialysis. The main advantage of membrane systems is that there is no need to add additional chemicals to separate pollutants from water, and since the membranes act as filters, energy consumption can be kept low. The microfiltration process uses membranes with a pore size of 0.1-10 µm and these membranes remove all bacteria. Microfiltration is applied to remove suspended solid particles from well water or pre-treated wastewater (e.g. in chemical-physical systems). Microfiltration systems are often used as pre-treatment for reverse osmosis, nanofiltration and ultrafiltration systems. Ultrafiltration systems with ceramic membranes (alumina or silicon carbide) are mainly used to separate medium-high molecular weight compounds. The advantage of ceramic membranes is that they are resistant to various types of pollutants and can be washed with different chemicals and at high temperatures. Nanofiltration systems differ from reverse osmosis systems in the type of membrane installed. Nanofiltration is mainly applied for the removal of

organic substances (dyes, nitrates, etc.) and multivalent ions. Nanofiltration membranes can also be used for the filtration of aqueous solutions with the aim of recovering process fluids by separating waste substances. Other applications are downstream of waste water pre-treated with chemical-physical systems or evaporators. The reverse osmosis process does not simply consist of a physical obstacle (determined by the size of the membrane pores) to the passage of molecules, but exploits the different chemical affinity of the species with the membrane, allowing, in fact, the passage of hydrophilic molecules, that is, chemically similar to water, with an efficiency of 98%. The membranes used in reverse osmosis are generally made of polyamide and are usually used: for the production of demineralized water, for the desalination of brackish water and for the treatment of wastewater in order to recycle the purified water.

DISINFECTANTS UV

Disinfection is the removal and killing of pathogenic microorganisms (viruses, bacteria, protozoa) and is the last stage of a water purification treatment, unless it is needed after a further dechlorination treatment [34,35]. The disinfectants used are: chemical, physical (UV), natural (slow sand filtration, phytoremediation and biological treatment). The disadvantage of using UV is that it is rendered inactive by the presence of turbidity, while the advantage is that all other disinfectants produce by-products except UV rays. UV disinfection instantly neutralizes microorganisms that pass through ultraviolet lamps immersed in the effluent and is a technology that has increased considerably in recent decades. In new wastewater treatment plants built around the world, UV rays are increasingly selected for disinfection due to the reduction in both investment costs and long-term operating costs. Furthermore, UV is an effective disinfectant for chlorine-resistant protozoa, such as *Cryptosporidium* and *Giardia*.

CHEMICAL PURIFICATION

In this paragraph are reported informations in ref [1-19] and also in ref [36-53] specifics for the several technologies of chemical purification. In this second paragraph we will consider the chemical treatments for water purification that are carried out both upstream and downstream of the biological treatment, they are the following: the clariflocculation, to eliminate non-sedimentable solids by adding chemical substances; the chemical precipitation, in the primary of ions and anions that can be toxic for the biological

and in the tertiary to break down phosphates; the chemical oxidation to eliminate non-biodegradable organic substances in the tertiary and oxidize inorganic substances to facilitate their subsequent elimination in the primary; the reduction of inorganic substances and chemical adsorption to facilitate their elimination in the primary; ion exchange on resins and zeolites to eliminate cations and anions in the primary, electro dialysis to eliminate ions with membranes and electrodes in the primary and tertiary and finally chemical disinfection in the tertiary.

CLAIRFLOCCULATION

Clairflocculation is a chemical-physical treatment used to eliminate turbidity, colloids, colors and facilitate the precipitation of suspended substances that cannot be settled, forming aggregates of larger size and weight until they form a precipitate [36-37]. Clairflocculation consists of the following phases: 1) coagulation, i.e. the destabilization of colloidal substances; 2) flocculation, i.e. the agglomeration of destabilized particles that can then be more easily sedimented; 3) clarification or sedimentation/precipitation of solids (physical processes already discussed in the previous paragraph. While in the primary sector, clariflocculation is used to eliminate substances that require a long time to precipitate, in the tertiary sector the aim is to remove biodegradable substances and residual microorganisms from the treated water. In clariflocculation, coagulants are added first and then a "coagulation aid" or "flocculant" which promotes further destabilization of the colloidal particles. In the coagulation stage, the cations deriving from the coagulants used interact with the negatively charged surface that covers most of the colloidal substances which are usually coated with negative charges. The aids used are: $Al_2(SO_4)_3$, $AlCl_3$, $Al_n(OH)_mCl_{3-n-m}$, $FeCl_3$, $Fe_2(SO_4)_3$, $FeSO_4$, $Ca(OH)_2$ and CaO . Flocculation consists in the addition of flocculants which facilitate the agglomeration of destabilized particles into microflakes and then into coarse flakes that precipitate easily. Flocculants are substances of various origins that exert their action in well-defined pH range values and are generally: 1) inorganic electrolytes or organic polyelectrolytes; the most commonly used are organic macromolecules obtained through polymerization processes, soluble in water or well dispersible, characterized by the presence of ionic groups along the entire chain; 2) polymers that present numerous polar groups along their chain. In fact, the presence of ionic

groups or polar groups, uniformly distributed along the chain of these flocculant polymers, facilitates the aggregation of multiple microflakes to the chain, forming larger flakes. There are numerous substances used as flocculants, such as activated silica, fine siliceous sand, diatomaceous earth, clay, bentonite, powdered activated carbon, starches, polysaccharides and alginates, synthetic organic polymers such as polyacrylamide. The alternative technology to clariflocculation is ultrafiltration with membranes.

CHEMICAL PRECIPITATION

Chemical precipitation consists in the reduction of inorganic cations and anions by adding a precipitant and is carried out both in primary treatments to eliminate substances that can create problems in biological treatment, and in tertiary treatments, but only to reduce phosphates (which are used in biological treatment and cannot be eliminated beforehand) [38-40]. Cations are precipitated by adding anions OH^- , S^{2-} , CO_3^{2-} and SO_4^{2-} , with the formation of hydroxides, sulphides, carbonates and sulphates. Anions are precipitated by adding Ca^{2+} ions or mixtures of Ca^{2+} , Al^{3+} , Fe^{2+} and Fe^{3+} . The operations that accompany precipitation are the following: precipitation can be preceded by the elimination of cation chelating substances like cyanides and NH_4^+ ; precipitation can be preceded by the reduction of ions that are not easily precipitated, such as Cr^{6+} to Cr^{3+} or oxidation of As^{3+} to As^{5+} ; precipitation can occur at variable pH to precipitate individual cations at pH between 7 and 11, for example pH 7 for Cr and pH 10.5 for Zn and Cd; the treatment is completed by a further phase of clarification-flocculation and final filtration or can be carried out simultaneously. Chemical precipitation is used: in the softening of primary water (precipitation of Ca^{2+} and Mg^{2+}); in the elimination of heavy and/or toxic metals and also in their recovery especially in the treatment of wastewater from metallurgical industries; in the elimination of ions that can inhibit biological oxidation; in the elimination of phosphates after biological treatment. The effectiveness of precipitation depends on the concentration of the ion and is useful when it is high, on the pH, on the absence of substances that can inhibit precipitation (cyanides and NH_4^+ ion), on the times required and on the composition of the mixture. For example, phosphate precipitation occurs by adding iron salts (FeSO_4 , FeCl_2 , FeCl_3), aluminum salts [$\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$], lime [$\text{Ca}(\text{OH})_2$] with formation of $\text{Ca}_3(\text{PO}_4)_2 \cdot 6(\text{OH})_2$, FePO_4 and AlPO_4 . Alternative methods to chemical precipitation

to eliminate toxic ions and cations are: reverse osmosis, ion exchange, chemical adsorption filtration, electrochemical removal and distillation; only for phosphorus is only partial biological removal and treatment with algae also used. Precipitation has the advantage of being cheaper than other techniques, but produces greater quantities of solid waste.

CHEMICAL OXIDATION PROCESSES

These treatments consist of the oxidation of organic and inorganic substances [41]. The types of chemical oxidation have the following names: 1) disinfection, which is only partially an oxidation and will be discussed in a subsequent paragraph; 2) chemical oxidation, which is an oxidation by direct interaction of the oxidant with the substances to be oxidized and is used mainly in the treatment of primary waters; 3) advanced oxidation (AOP), which is an indirect oxidation by formation of $\bullet\text{OH}$ radicals, which are the strongest oxidants and is used to completely eliminate substances present in waste water; 4) ozonolysis, which is the use of O_3 and is so called only the direct interaction of O_3 with recycled sludge of biological oxidation, while O_3 is also used as an oxidant in the other three sectors mentioned above. The oxidative treatment has the following different locations: before the biological treatment to eliminate negative substances, for example the oxidation of sulphides, Fe^{2+} and Mn^{2+} ions and the elimination of cyanides, sulphides, nitrates and to increase the biodegradability of the organic substances present; after the biological treatment to completely oxidize the non-biodegradable organic substances; simultaneously with the biological treatment to transform organic substances into CO_2 in the recycling of sludge and reduce their production.

The treatment called "chemical oxidation" is carried out by direct interaction of the pollutants to be eliminated with the following substances (Cl_2 , ClO_2 , O_3 , NaClO , H_2O_2 , KMnO_4 , O_2 , O_2/MnO_2 , $\text{Mn}^{2+}/\text{oxalic acid}/\text{O}_3$) and is used to oxidize non-biodegradable organic substance by transforming them into biodegradable ones and to oxidize inorganic pollutants. Alternative treatments to chemical oxidation are: adsorption on activated carbon and membrane filtration. Advanced oxidation is based on the chemical oxidation of pollutants by means of highly reactive radical species ($\bullet\text{OH}$) that allow the degradation of a wide range of organic compounds into intermediates of lower molecular weight, potentially up to their complete mineralization. Advanced chemical oxidation is carried out with mixtures of oxidants and/or UV radiation:

H_2O_2/UV ; O_3/UV ; $H_2O_2/O_3/UV$; H_2O_2/O_3 ; H_2O_2/Fe^{2+} (Fenton); H_2O_2/Fe^{2+} (or Fe^{3+})/UV (Photo-Fenton); $TiO_2/h\nu(UV)/O_2$, photo-oxidation. Advanced chemical oxidation is used to oxidize all organic substances, even the most recalcitrant ones, such as drugs, pesticides, aromatics, chlorinated substances, to simpler biodegradable substances, even to the point of forming CO_2 , and to oxidize inorganic substances, both before and after biological oxidation. Some examples of $\bullet OH$ radical formation are given: $h\nu O_3 + H_2O \rightarrow 2\bullet OH + O_2$; $H_2O_2 + h\nu \rightarrow 2\bullet OH$. "Ozonolysis" is performed only with O_3 and is used to treat sewage sludge in order to reduce its volume and/or enhance biogas production. This treatment is performed on recycled sludge in the biological oxidation reactor. An aliquot of re-circulated sludge is collected and sent to an ozonolysis plant, which is a cellular lysis process capable of significantly reducing sludge production.

CHEMICAL REDUCTION

Chemical reduction is used to transform pollutants, so that they can be eliminated more easily [42]. The most commonly used reagents are: sulfur dioxide, sodium bisulfite/sodium metabisulfite, ferrous sulfate, sodium sulfide and sodium bisulfide, urea or amidosulfonic acid. An example of the application of chemical reduction in water purification is the reduction of Cr^{6+} to Cr^{3+} with sodium bisulfite, or ferrous sulfate or sodium sulfide. Another example is the reduction of Se^{6+} to Se^{4+} with ferrous hydroxide. Another reductant used for Se^{6+} is iron in the presence of copper ions. Elemental iron reduces both selenium and copper and produces a copper selenide on the surface of the iron.

CHEMICAL ADSORPTION

An example of water purification by chemical adsorption [43] is the removal of Se^{4+} by adsorption on ferrierite (zeolite) at pH lower than 8. Another chemical adsorbent used is activated alumina (high surface area) to remove mainly arsenic and fluorides from drinking water. Alumina is also used in the final treatment of wastewater from glass, aluminum, steel, semiconductor, pesticide and fertilizer industries.

ION EXCHANGE

Ion exchange is a chemical adsorption process and consists in the elimination of cations and anions from aqueous solutions or in the recovery of valuable cations by adsorption on solids by ion exchange, in particular with H^+ or Na^+ and OH^- ions present in solids (polymer resins or zeolites). The exchange

solids can be present in adsorption columns or in filters or in powder in aqueous suspension of water. Resins and zeolites are subsequently regenerated by exchange with $NaOH$ and HCl or H_2SO_4 . The solids used in ion exchange treatments are many and are the following: strongly acidic resins based on sulfonic resins $R-SO_3H$ for the total removal of cations; weakly acidic resins based on carboxylic resins $R-COOH$ for the partial removal of cations; strongly basic resins based on quaternary ammonium compounds R_3-N-OH for the total removal of anions; weakly acidic resins based on primary or secondary amines ($R-NH_3-OH$, R_2-NH_2OH) for the partial removal of anions; mixed anionic and cationic resins for the elimination of all ions; chelating resins based on strong cationic resins with $R-EDTA-Na$ groups for the selective removal of heavy metal cations; silicoaluminate-based zeolites (chabazite, clinoptilolite) which are Na^+ and H^+ cation exchangers for the removal of all cations (including NH_4^+). The use of ion exchange resins is as follows: water softening (removal of Ca^{2+} Mg^{2+} with Na^+) removal of Fe^{2+} and Mn^{2+} from groundwater with Na^+ ; recovery of expensive metals U, Ag, Au; demineralization of water by eliminating all cations and anions by replacing them with H^+ and $-OH$; desalination of water; production of ultrapure water by eliminating all present ions; decarbonization, i.e. the removal of CO_3^{2-} , HCO_3^- ions; removal of nutrients NO_3^- , NH_4^+ , PO_4^{3-} ; removal of radioactive ions Sr, U, Cs+; passage from large volumes of water to small volumes of solid; removal of heavy metals Pb, Ni, Cu, Cd and K; removal of anions F^- , Cl^- , SO_4^{2-} , arsenates, selenates, cyanates, bisulphites, perchlorates and chromates. Chelating resins are strong cationic resins, which can selectively capture only heavy metal cations. The chelating property is generally carried out by the presence of EDTA in the form of disodium salt on the resin, which exchanges its hydrogen ion with the metal to be removed. Cations with a high environmental impact, which can generally be removed with this type of resin are Cu^{2+} , Ni^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+} . The phases of ion exchange are the following: the first phase is exhaustion, in which the resin captures the polluting ions in solution until saturation, releasing the functional ones with the same electrical charge; the second phase is regeneration, in which the adsorbed polluting ions must be eluted and replaced with the ion initially present on the resin. It is necessary to use at least two ion exchange columns working in parallel and with alternating regenerations. The factors that influence the efficiency of ion exchange are: pH, temperature, the presence of other ionic species, their concentration, the

presence of possible oxidizing agents of the polymers and the quality of regeneration. The advantages of ion exchange resins compared to reverse osmosis are the following: better quality of the water produced; lower water consumption (the incoming water is completely demineralized, without waste); lower electricity consumption. The negative characteristics of resins are the following: there is no absolutely selective resin, the removal occurs not only of a specific ion, but also of the other ions present in the water; the deactivation of the resins; the presence of organic matter of which the resins are made can favor bacterial proliferation, therefore for water for human consumption it is necessary to install a disinfection system; if organic substances are present, which can contaminate the ionic resins, it is necessary to insert a granular carbon filter placed before the resin filters; production of regeneration eluates intended for purification; consumption of acid and soda reagents for regeneration and sulphates or chlorides; need for a double line for continuity of operation; deactivation of resins. The deactivation of ion exchange resins occurs: due to mechanical wear (pulverization and consequent loss of a part of the resin 4-5% per year); due to chemical poisoning (due to free chlorine that oxidizes or to the presence of some ions, such as iron, which are very similar and bind to the resin in an irreversible way); due to the lack of adequate pre-filtration, which can cause the resins to foul; due to blockage caused by organic material. The waste water produced in the regeneration process (water polluted by high concentrations of chlorides) is highly polluted and its disposal creates problems and is the cause of the abandonment of this technology in favor of treatments with a lower environmental impact, such as reverse osmosis. The most widespread application of ion exchange is water softening, for the removal of hardness to lower the concentration of calcium and magnesium. Seawater treatments consist of membrane systems coupled with ion exchange systems. Demineralization processes are carried out with the following phases: the water is pre-treated with reverse osmosis to reduce the total salt content by more than 90%; then it is treated with anion and cation exchangers. Ultrapure water is used for the pharmaceutical, electronic and semiconductor industries and is obtained in a first stage by ion exchange or reverse osmosis and in a second stage with mixed bed resins or an electro-deionizer. The decationizers are composed of a quartz sand or activated carbon filter and a cation resin filter. Alternative technologies to ion exchange to remove ions from water are the following: reverse osmosis

(desalination), distillation, freezing, electrodialysis and precipitation. Ion exchange is effective for treating very dilute solutions and for achieving complete removal of ion.

ELECTRODIALYSIS

Electrodialysis allows the removal of only ionic species, it is particularly suitable for the treatment of wastewater from the galvanic industry and metal finishing processes [48-50]. An electrodialysis cell consists of an anode and a cathode separated by cationic membranes (permeable only to cations) and anionic membranes (permeable only to anions). The liquid, introduced between the membranes, is subjected to the electric field that diverts the ions present in solution towards the electrodes (depending on the sign of their charge); in this way, thanks to the appropriate arrangement of the selective membranes, a concentrated flow and a diluted flow are formed.

DISINFECTION

Disinfection or sanitization consists in the removal, deactivation and killing of pathogenic microorganisms (viruses, bacteria, protozoa) that cause diseases and is generally the last stage of a water purification treatment, unless it is needed after a further dechlorination treatments [51-53]. Sterilization, on the other hand, is a treatment intended for the complete elimination or destruction of any form of microorganism, pathogenic and non-pathogenic including spores. Disinfectants can be chemical, physical (UV) or natural (slow filtration on sand, phytoremediation and lagooning). Chemical disinfectants are: Cl_2 , ClO_2 , NaClO , $\text{Ca}(\text{OCl})_2$, O_3 , $\text{CH}_3\text{C}(\text{O})\text{OOH}$, NH_2Cl , NHCl_2 . The greatest quantity of pathogenic microorganisms is removed in primary, secondary and tertiary treatments and many are solids in suspension; for this reason they are largely eliminated in the clarification-flocculation and filtration processes. At the end of all these stages, pathogenic microorganisms may remain from 2 to 10%, and some may also form during the various treatments. Their total elimination occurs in the last stage, that of disinfection. The action of disinfectants on the structure or vital functions of pathogenic microorganisms to eliminate them is due to multiple actions, not only to the oxidizing power, such as: damage to the cell membrane, alterations in membrane permeability, alterations in cell protoplasm, alterations in DNA or RNA, inhibition of enzymatic activity. The problems of all chemical disinfectants are the production of by-products, furthermore chlorine is toxic and requires a

downstream dechlorination plant; for this reason chlorination is not recommended, in particular the chlorine at the outlet is reduced or adsorbed on activated carbon. Ozone has the disadvantage that it can form aldehydes and ketones and is expensive. The disadvantage of UV is that it is inactivated by the presence of turbidity; O_3 and ClO_2 are considered the best disinfectants, followed by peracetic acid, while chlorination is effective against viruses and bacteria, but not against cysts and protozoan oocysts. ClO_2 does not give rise to organic chlorinated compounds but to chlorites, chlorates and dichlorates, toxic but unstable substances.

BIOLOGICAL TREATMENTS

In this paragraph are reported information taken from references [1-19] and also from [54-67] that are specific of this paragraph.

Biological treatments, which are the most important ones for the purification of civil and industrial wastewater are used to eliminate biodegradable organic substances and compounds that contain nitrogen and in small percentages phosphates, always require a primary treatment to eliminate the substances that are negative for the biological treatment and a subsequent one to remove the substances not removed with the biological treatment. The treatments that accompany the biological treatment are: denitrification, carried out in the absence of O_2 , nitrification and oxidation, carried out in the presence of O_2 , post-denitrification, carried out in the absence of O_2 and post-aeration carried out in the presence of O_2 . These treatments are always followed by flocculation, sedimentation/decantation and sludge filtration. The biological treatment consists of: a) the biodegradation by microorganisms of organic substances present in the water to be purified by oxidation, until they are transformed into simpler and environmentally harmless substances and, finally, into CO_2 ; b) the transformation of ammonia by oxidation into nitrates and after reduction into nitrogen; c) the transformation of dissolved organic substances present in colloidal form into sedimentable compounds; d) an increase in the quantity of microorganisms that go into the sludge following the consumption of organic substances; e) the formation of gas; f) in the formation of aggregates of organic matter and microorganisms in the form of flakes.

The purification mechanism is based on the degradation of organic substances by bacteria and microorganisms, using

the oxygen dissolved in wastewater or oxygenated organic substances. The types of microorganisms used are mainly protozoa (flagellates, amoebae, ciliates), some metazoa (nematodes, rotifers and gastrotrichs, oligochaetes and tardigrades), and also bacteria, flagellated algae and fungi. They have the following functions: degradation, which consists in the oxidation of organic carbon; flake-formers; nitrifying-denitrifying and other genera that degrade carbon compounds using oxygen or even nitrates and nitrites as electron acceptors (anaerobic respiration); phosphorus-accumulators; filamentous and sulphur-oxidizers. BOD_5 (Biochemical Oxygen Demand) and COD (Chemical Oxygen Demand), are used as indicators for biological treatment. BOD_5 , expressed in mg/l of O_2 , represents the quantity of O_2 that is used in 5 days (120 hours) by aerobic microorganisms (inoculated or already present in the solution to be analyzed) to decompose (oxidize) the organic substances present in a litre of water or aqueous solution in the dark and at a temperature of 20 °C. BOD is therefore an indirect measure of the content of biodegradable organic matter present in a sample of water or aqueous solution. COD expressed in mg/l of O_2 , represents the quantity of oxygen necessary for the complete chemical oxidation of the organic and inorganic compounds present in a water sample.

Biological treatment is carried out when the optimal COD/BOD ratio is 1.9-2.4 using good stirring. The alternatives to biological treatment are membrane treatment and chemical oxidation, when the COD/BOD ratio > 4, and natural treatment (phytoremediation and biological treatment). Phytoremediation represents an advantageous alternative, not only from an environmental point of view, but also from an economic one, especially in rural areas. The basic principle of the process involves the cultivation of aquatic plants on a suitable growing medium. The polluting elements become nutrients for cultivated plants and allow purified water to be returned to the environment, this is a process that requires a lot of space and is slow, therefore it is not applicable in all circumstances. The optimal conditions for biological treatment are the following: temperature 25-30 °C; the oxygen level must not drop too much, the ideal is to use oxygen and not air; there must be nutrients N and P there must be no toxic and inhibitory substances such as heavy metals (Cr, Ni, Cu, etc.) and toxic organic substances (insecticides, pesticides, fungicides, etc.) and salts:

BIOLOGICAL TREATMENT PLANTS

Biological treatment plants are the following: suspended biomass, adhered biomass, use of MBR reactors (Membrane Biological Reactor), use of MBBR reactors (Moving Bed Biofilm Reactor). Suspended biomass plants (activated sludge) all have, after the activated sludge treatment, the sedimentation and filtration phase to recycle the biological sludge partly in the first sedimentation tank, partly in the oxidation tank and partly disposed of after appropriate treatments. The bacterial populations are present in the form of flocs kept in suspension by air insufflation (if aerated reactors) or by stirrers (if anoxic or anaerobic reactors). Suspended biomass plants are currently the most used system due to their high efficiency (>90% BOD5 removal). The activated sludge reactors with discontinuous cycle operation called SBR reactors (Sequential Batch Reactor) are discontinuous flow treatment systems capable of incorporating the different treatment phases in a single basin, they are not like traditional activated sludge systems, in which the flow passes from one tank to the next, but are processes that occur in a single tank, with variations in the flow and volume of the tank. The systems built with SBR technology are particularly suitable for the treatment of domestic wastewater from small and medium-sized communities and in particular industrial wastewater, as they are not very sensitive to variations in hydraulic and organic load. The use of oxygen instead of air for oxygenation allows for greater treatment of wastewater, reduces problems related to the formation of foam, odors and volatile emissions and, therefore, treatment capacity for the same volume used. The attached biomass systems are with trickling beds, biological discs or biofilters, in which the bacterial biomass grows remaining attached to a surface. These systems are divided into two technologies, fixed support and mobile support. In fixed support systems, the sewage flows through trickling beds. In mobile support systems, such as biological disc systems, the support moves semi-immersed in the sewage. Adhered biomass systems do not require sludge recirculation to ensure the appropriate concentration of activated sludge in the bioreactor. The MBR (Membrane Bio Reactor) system is a biological water purification system that consists of the combination of the traditional activated sludge purification process and a membrane separation system (generally microfiltration or ultrafiltration) that replaces the normal secondary sedimentation tank. MBBR (Moving-Bed Biofilm

Reactor) systems are adhered biomass reactors, the activated sludge present in the reaction compartment is not suspended in the water to be treated, but adheres to a series of plastic and mobile supports inside the biological reactor. These support media are made of plastic material, with a density close to that of water, and are kept in suspension. Nitrogen elimination occurs with the following treatments: pre-denitrification, oxidation and nitrification, post-denitrification and post-aeration. Pre-denitrification is a process of nitrate reduction by bacteria in an anoxic environment. Denitrifying microorganisms, by metabolizing the organic substance, use the oxygen of nitrates as a source, reducing the latter to nitrogen. Anaerobic processes produce gas (CH₄, CO₂, H₂S) and develop less sludge.

The oxidation-nitrification treatment receives the water from pre-denitrification and this treatment occurs in a tank with aerobic and nitrifying microorganisms. By means of a system of compression and distribution of air in microbubbles, the microorganisms are supplied with the oxygen necessary for the metabolization of organic substances and the oxidation of ammonia contained in the sewage: the oxidation-nitrification process determines bacterial growth and therefore the production of biological sludge. In the post-denitrification phase, the same process as pre-denitrification occurs, with reduction of nitrates by means of denitrifying bacteria in an anoxic environment. A hydroalcoholic mixture is added to the tank as a source of organic carbon and the denitrifying microorganisms, metabolizing the organic substance, use the oxygen of the nitrates as a source, reducing the latter to nitrogen. The post-aeration phase consists of subjecting the water to aeration by means of microbubble diffusers to re-establish aerobic conditions and oxidize the last residues. The sludge obtained in the purification of water with biological treatment goes for 16% to incinerators, for 46% to the rural sector, while 38% is placed in landfill.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

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