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Removing ammonium from water intended for human consumption. A review of existing technologies

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Removing ammonium from water intended for human consumption. A review of existing technologies

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Abstract. Ammonium is an inorganic compound present in water at $\text{pH} < 9$. Ammonium has no toxic effects on human health, but its presence in water can indicate a water pollution. The presence of ammonium in groundwater source can be largely determined by the reducing conditions from the aquifer, while in surface water sources it is found only in polluted waters. In water supply systems, the presence of excess ammonium in raw water is not desirable because it can generate problems such as: unpleasant odors, microbial development in the water distribution system, reducing the efficiency of chlorine disinfection and increased chlorine consumption. Over time, several methods have been developed to reduce the concentration of ammonium from water, these being physical, chemical, biological or a combination of these methods. The article presents a review of the technologies currently used to reduce /oxidize ammonium from water. These mainly includes: ion exchange and adsorption, biological filtration, air stripping, breakpoint chlorination and reverse osmosis.

1. General data

Ammonium is an inorganic compound, present in water at $\text{pH} < 9$. Ammonium has no toxic effects on consumers' health, but its presence in water may indicate water pollution. In groundwater, the presence of ammonium in water can be largely due to reducing conditions in the aquifer, and in surface water sources, it is found only in polluted waters. Ammonium must be reduced/oxidized in drinking water because it is a nutrient that can allow the growth of certain bacteria in water distribution systems [1].

In water supply systems, the presence of excess ammonium in raw water is undesirable because it can cause many problems such as: unpleasant odors, microbial development in the water distribution system, reduced efficiency of chlorine disinfection and increased chlorine consumption [2], [3]. It reacts with chlorine used in water disinfection leading to degradation of water quality by changing its taste and smell [4], [5].

Ammonium is an important source of nitrogen for mammals and plants due to its use in the synthesis of amino acids, DNA, RNA and proteins. It is an endogenous product in all mammalian species. In the natural environment, ammonium comes from both natural and anthropogenic sources [6].

The assessments made by the World Health Organization on ammonium in water, reconfirmed the conclusions of previous studies, resulting that the exposure to ammonium from the environment is insignificant compared to the endogenous synthesis of ammonium. Toxicological effects are observed only when ammonium exposure is greater than 200 mg/kg body weight [6].

In Romania, the maximum allowable limit for ammonium in drinking water, according to law 458/2002 is 0.50 mg/l. The guideline level for ammonium, according to the World Health Organization (WHO 1993) is 1.5 mg/l.



Over time, several methods have been developed to reduce the concentration of ammonium in water, namely physical, chemical, biological methods or a combination of these methods. These mainly include: ion exchangers and adsorption, biological filtration, air stripping, breakpoint chlorination and reverse osmosis [7].

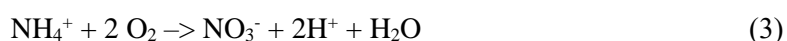
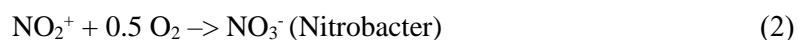
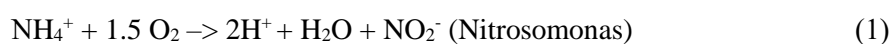
2. Biological process

2.1. Nitrification

The biological process of ammonium oxidation to nitrate with the intermediate form of nitrite, is called nitrification. The nitrification process is realised by a specific bacterial population, the main 2 known species of bacteria are *Nitrosomonas* and *Nitrobacter* [8]. These specific bacteria are distinguished from each other by the ability to oxidize only certain nitrogen compounds. While *Nitrosomonas* can oxidize ammonium to nitrite, *Nitrobacter* oxidizes nitrite to nitrate. These 2 specific species of bacteria are classified as autotrophic organisms (they do not need a source of organic carbon, they use carbon dioxide for synthesis) [9]. At the biochemical level, the process involves more than a continuous oxidation of ammonium to nitrate, because many intermediate reactions and enzymes are involved in the process. It is very important to know the behavior of nitrifying organisms or microorganisms in different environmental conditions, because knowing the optimal conditions for the development of nitrifying bacteria leads to the development of systems in which they can effectively perform their metabolic activity [10].

Nitrosomonas and *Nitrobacter* are present everywhere in the soil, in water basins, in wastewater treatment plants and in landfills.

The stoichiometric equations of nitrification for *Nitrosomonas* and *Nitrobacter* are [9]:



The above equation represents the compound equation of oxidation of ammonium to nitrate made by the 2 species of bacteria.

The nitrification process is influenced by certain inhibitory factors such as pH, dissolved oxygen concentration, temperature and inhibitors [9].

The nitrification process takes place at temperatures between 4 and 45°C, with an optimal temperature of 35°C for *Nitrosomonas* and an optimal temperature of 35-42°C for *Nitrobacter*. An increase of temperature by about 10°C, leads to doubling the growth rate of microorganisms. (Ex: at a temperature of 10°C, the growth rate of microorganisms is equal to 0.3 [day⁻¹] and at a temperature of 20°C, the growth rate of microorganisms is equal to 0.6 [day⁻¹]) [10].

For the nitrification process to work optimally, it is recommended that the minimum level of dissolved oxygen concentration be 2 mg/l. The presence of oxygen is a mandatory requirement for all species of nitrifying bacteria, in the absence of oxygen the ammonia oxidation reactions take place at a slow pace or stop completely [9], [10].

For functioning of the nitrification process, it is recommended that the pH be maintained in the range of 6.5-8, with an optimal pH of 7.2.

Nitrifying bacteria activity can be affected (inhibited) by inorganic compounds such as zinc, nickel, percolate, hydroenzyme, as well as by organic compounds such as ethylamines, phenol [9].

2.2. Denitrification

Denitrification is the biological process of reducing nitrate to nitrogen gas in several stages with the help of denitrifying bacteria [8].

In the case of denitrification, nitrate replaces dissolved oxygen in bacterial respiration, so denitrification occurs in the presence of nitrate and in the absence of dissolved oxygen (anoxic conditions).

Unlike nitrification, a process performed by specific bacteria, denitrification is realised by a large number of bacteria, over 75 different genera. Denitrifying bacteria are ubiquitous in many environments, and this is due to the fact that they are optionally aerobic/anaerobic, respectively they can use both oxygen and nitrate as a source of electrons [10].

Depending on the nature of the donor electron (respectively of the substrate), used for the energy and/or cellular synthesis of denitrifying bacteria, donor electron that can be organic or inorganic, the bacteria involved in the process can be heterotrophic or autotrophic bacteria [10].

Heterotrophic denitrifying bacteria require a source of organic carbon for multiplication. If there are not enough dissolved organic substances in the water, added substances can be used, such as methanol, ethanol, acetic acid, etc. [10].

To reduce nitrate, autotrophic denitrifying bacteria do not need an external source of organic carbon, because in autotrophic denitrification, hydrogen or reduced sulfur species act as substrate and carbon dioxide or bicarbonate is used as the source of organic carbon for cell synthesis [10].

The denitrification process is influenced by certain inhibitory factors such as temperature, dissolved oxygen concentration, pH and alkalinity, inhibitors and the ratio between electron donor and nitrogen [10].

Denitrification is influenced by dissolved oxygen, with a maximum optimal concentration of 0.2 mg/l. Above this concentration it is considered that the denitrification process stops, but in practice it is considered that the denitrification stops only if the concentration of dissolved oxygen is higher than 0.3-0.5 mg/l [9], [10].

In the denitrification process the rate of nitrate reduction is influenced by temperature. At a temperature drop below 20°C, the process is more influenced than at temperatures higher than this [9], [10].

The denitrification process is affected by pH and alkalinity, because bicarbonates are produced in the process. The alkalinity produced is 3.57 mg alkalinity expressed in CaCO_3 , produced per mg of nitrogen from nitrate reduced to nitrogen gas [9]. Because alkaline substances are formed in the process, the pH can increase depending on the amount of nitrate reduced. Denitrifying bacteria are not particularly sensitive to pH, but pH values outside the range of 7-8.5, can lead to accumulations of intermediate by-products such as nitrates, nitric oxide and nitrous oxide [10].

Denitrifying bacteria are more sensitive to inhibitory compounds, for this reason the ability of biomass to acclimatize to higher concentrations of inhibitory substances must be taken into account [10].

2.3. Biofilters.

The main biological processes used to reduce ammonium in raw water are mainly processes with attached biomass. Biofilters are characterized by the presence of microorganisms that adhere to the support medium in the form of a fixed film (biofilm) [11].

Regardless of the support medium used, all filters follow the same principle, namely: biological degradation of pollutants by microorganisms fixed on the surface of the support medium.

In natural and artificial systems, suspended microbial cells are transported by a flow of fluid to the surfaces where they can attach.

Under favorable environmental conditions, the absorbed cells grow, multiply, and produce extracellular polymeric substances that bind the cells together. Aggregates related to extracellular polymeric substances and other substances accumulated on surfaces are called biofilters.

The performance of the filter depends on the microbial activity, meaning a constant amount of substrate (organic substances and nutrients) is required for the operation of the biofilter. In the activity of a biofilter there are 3 important processes, namely the fixation of microorganisms, the development of microorganisms and the detachment of the film from the support [10].

The efficiency of a biofilter also depends on the type of support medium used, medium that represents the support for the growth of bacteria. Initially the biofilters were filled with gravel or sand but a sufficiently rigid basin was needed to withstand the weight of the support medium and water. More recently, the most used support media are plastics, ceramics and synthetic fillings. The properties of plastic substrates are: specific surface of the substrate, three-dimensional distribution of the surface, free volume (free space inside the substrate through which water flows) and resistance to clogging, ease of cleaning the substrate, rigidity, aging of the raw material (resistance in time of the support environment) and weight [10].

2.3.1. Classification of submerged biofilters. Depending on the supply mode, submerged biofilters can be:

- Upflow biofilters;
- Downflow biofilters.

Submerged downflow biofilters are usually with fixed bed and use a variety of support materials. The main advantages of such a filter are given by the fact that when using a support media with a large volume of voids, clogging problems are avoided and are relatively easy to operate [8].

Submerged upflow biofilters, depending on the degree of expansion of the bed can be:

- With fixed bed;
- With fluidized bed;
- With expanded bed;

Upflow biofilters with fixed bed - are used at low upstream speeds to prevent biomass washing. They are easy to operate and use as support media: corrugated plastic modules, tubular modules and bulk materials [10].

Upflow biofilters with expanded bed - for operation with bed expansion of approximately 20%, is used an ascending speed of approximately 2 m/h. Usually the support medium used is sand with a granularity of 0.2-0.5 mm [10].

Upflow biofilters with fluidized bed - are similar to those with expanded bed, only they work at ascending speeds of about 20 m/h, to ensure a 100% expansion of the bed. The main advantage is that they are very resistant to pollutant loading shocks [10].

2.3.2. Nitratur. It is a biological process with attached biomass, which ensures the reduction of ammonium and nitrates from water, because it is applicable either for nitrification (with the reduction of ammonium to nitrate) or for denitrification (with the reduction of nitrate to nitrogen gas) [1].

Nitratur N (Nitrification) - can be used either upflow, where the efficiency is maximum, or downflow, in which case the advantage is the more efficient retention of solids.). In the case of this biofilter, type Nitratur N, the support material used, which recorded the best performance is Biolite L. The nozzles plates that support the filter layer are provided with 2 types of nozzles, one is for water and one for air. The air introduced through the nozzles maintains a sufficient concentration of oxygen over the entire depth of the support medium. During backwashing, air and water are introduced simultaneously [1].

Nitratur D (Denitrification) - in this process are used bacteria that are not strictly aerobic and that use oxygen present in nitrates for their metabolism, meaning the process is anoxic. The support material is also Biolite L, and is used with upflow, because this flow direction helps to eliminate nitrogen gas, which is the final product of denitrification. Using with downflow would lead to the accumulation of nitrogen gas in the middle of the reactor, which leads to an increase of head loss [1].

2.3.3. Pozzolana filters. These are biofilters that use pozzolana as a support medium, because in most countries pozzolana is cheap. Pozzolana granularity must be greater than 1 cm [1].

Pozzolana is a natural siliceous or siliceous and aluminum material derived from primary deposits of volcanic ash. In the presence of water and at room temperature, pozzolana reacts with calcium hydroxide and form hydrated calcium silicate compounds and hydrated calcium aluminate compounds.

During operation, the head loss is slight, but if the filter reaches a level that no longer allows its proper functioning (it clogs), washing the filter layer is almost impossible. Two methods are used to wash this substrate, either by regular washing with chlorinated water to prevent bacterial growth and accumulation of biological sludge or by removing the filter medium once every 2-3 years for a more efficient washing and to prevent compaction of the media [1].

2.3.4. Slow sand filters. The slow sand filter is a sand filter operated at low filtration speeds, without using coagulation in pretreatment. The granularity of the sand is smaller than that used in a rapid filter, and this is a plus in the retention of solids, these being retained entirely in the biological membrane formed at the surface of the filter. This biological membrane, made up of dirt and alive and dead micro and macro-organisms, becomes the dominant medium in the filter as the filtration cycle progresses [12].

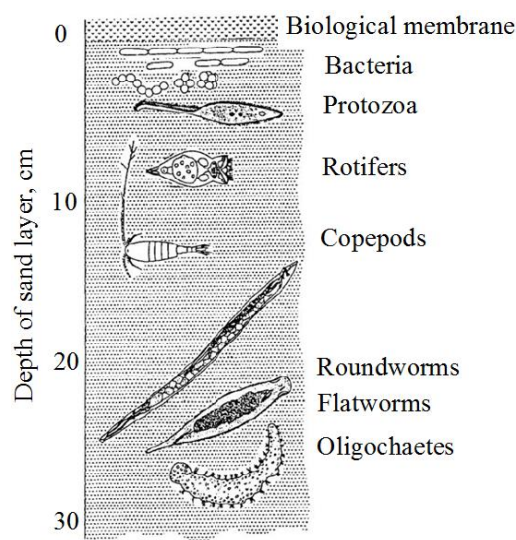


Figure 1. Slow sand filter [1].

The filter is cleaned when the pressure loss in the filter becomes excessive, by lowering the water level below the filter layer followed by the manual removal of the biological membrane formed on its surface, including 5-10 cm from the sand layer. Depending on the quality of the raw water, the duration of the filtration cycles can vary between 1 and 6 months [12].

The slow sand filter was developed in England in the 19th century and continues to be used successfully on the raw water of the River Thames, which serves London. Slow filtration is a simple technology and is mainly used for a good quality surface water source [12].

The removal mechanisms in a slow sand filter are both physical and biological. During the use of the filter, a biological membrane is formed on the surface of the filter and inside the filter layer. The efficiency of the filter improves after the first filtration cycles, as the biofilm develops. In addition, living organisms in the filter reduce the concentration of organic compounds and can promote chemical transformations, such as the oxidation of ammonium to nitrate [12].

Since the slow sand filter is partly a biological process, it is affected by temperature and pre-chlorinated raw water. At a free chlorine concentration of 6-12 mg/l in raw water, the filter efficiency decreases [12].

Reducing the concentration of ammonium in water using slow filters is very little used, because the efficiency of slow filters on this process is relatively low, requires very large spaces to make filters and until the formation of biofilm from the filter surface, ammonium can not be retained [12].

2.4. Reducing the ammonium concentration using biological processes

As a summary of what biological processes represent in reducing ammonium, it can be said that these are some of the most efficient processes, because ammonium can be reduced completely.

Numerous studies have shown that biological processes have a high efficiency in reducing ammonium, but are very expensive, difficult to operate and require special conditions for the development of microorganisms[13].

3. Membrane filtration

The membrane is a physical barrier with mesh dimensions that retains larger elements and allows passing of smaller elements.

The process is completely automated, does not require a permanent operator and is suitable in rural areas.

Membrane separation and concentration processes began to be applicable in treatment processes in 1960, through the development of synthetic membranes [14].

The membrane filtration process is defined as the action by which the flow of raw water is divided into permeate (contains water with substances that has passed through the membrane) and into concentrate/brine (contains salts and dissolved substances that have not passed through the membrane) [15].

A simplified scheme of a permselective membrane is shown in the following figure.

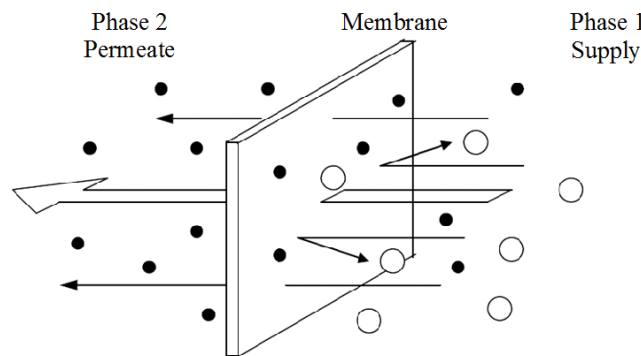


Figure 2. Simplified scheme of a permselective membrane [15].

The use of the membrane filtration process has the following advantages:

- Separation occurs at the temperature of the working environment;
- There are no accumulations inside the membranes and they can be used continuously until exhaustion;
- Separation does not require chemical reagents, resulting a good quality water and at the same time significantly reducing residual ions.

3.1. Clasification of membranes

Reverse Osmosis - The solvent of the solution is transferred through a dense membrane, chosen to retain salts and dissolved substances. To produce fresh water from saline, must be acted on the solution with a pressure at least twice the osmotic pressure. For sea water, a pressure of at least 5 - 8 MPa results [15].

Nanofiltration - retains multivalent ions in softening operations and controls organic substances. Poor retention for monovalent ions leads to lower osmotic pressure. The pressure used for Nanofiltration is 0.5 - 1.5 MPa [15].

Ultrafiltration - allows clarification and disinfection operations. The membrane is porous and allows the retention of large dissolved substances, all particles and microorganisms such as viruses and bacteria. The operating pressure is 50 - 500 kPa [15].

Microfiltration - is used to clarify water, because it allows the retention of macroparticles, membrane pores in case of microfiltration are larger than 0.1 μm . The working pressure is 50 - 500 kPa [15].

Electrodialysis - ions are transported through selective ion membranes under the influence of an electric field. Waters richer or poorer in salts can be obtained [15].

3.2. Reverse osmosis

The process is performed at pressures higher than the osmotic pressure (5-8 MPa), produces an ultrapure water that needs remineralization to become drinkable, because it practically retains all the elements present in the water (more than 95%). Usually the reverse osmosis process is performed on partial flows and the permeate obtained is mixed with raw water so that a remineralization of the water is not necessary.

Reverse osmosis uses the properties of semipermeable membranes, which allow water to pass through the membrane, while solids are retained, except for certain organic molecules very similar to those of water [1].

If a concentrated saline solution is separated from a more dilute solution by semipermeable membrane, the difference in chemical potential helps the passage of water from a low-potential compartment to a high-potential compartment for its dilution (natural osmosis). To stop this diffusion it is necessary to apply a pressure on the filtered fluid. In equilibrium, the pressure difference established in this way is known as osmotic pressure. The following equation presents the osmotic pressure depending on the concentration, temperature and constant of an ideal gas [1], [14].

$$\pi = \Delta C R T \quad (4)$$

π - osmotic pressure [Pa]

ΔC - difference in concentration [mol/m³]

mol/m³ = concentration [kg/m³]/molecular weight [kg/mol]

R - constant of an ideal gas [J/molK]

T - temperature [K]

Using the above equation for 2 similar solutions, having the same concentration but with different molecular weight, it resulted that the lower the molecular weight, the higher the osmotic pressure, as can be seen in the following figure [1].

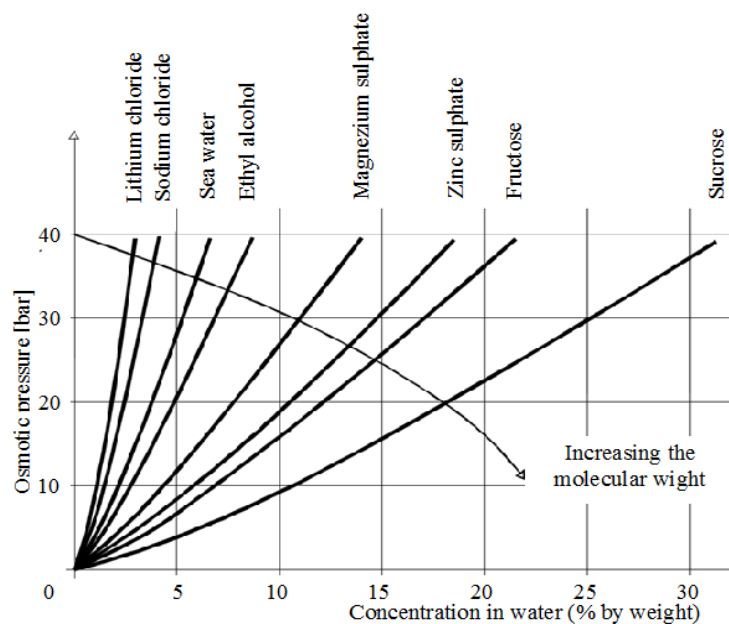


Figure 3. Osmotic pressure for different solutions [1].

In conclusion, in order to obtain a good quality water from a saline solution, the osmotic pressure of the solution must be exceeded [14]. For example, for a brine that contains several grams of salt / liter, pressures of 5-30 bar are required and for seawater pressures of 50 to 80 bar are required. There is

another consequence that can amplify the increase in osmotic pressure. When water is passed through the membrane, the molecules and ions retained by the membrane tend to accumulate on the membrane surface, increasing both the mineralization of the membrane-treated water and the osmotic pressure required to desalinate the solution. This phenomenon leads to increased energy costs and the risk of precipitation if the solubility of one of the cation-anion pairs is exceeded in the layer delimited at the membrane surface. This phenomenon is known as concentration polarization and it is defined by:

$$\Psi = C_m/C_e \quad (5)$$

C_m - concentration of the liquid in contact with the membrane,;

C_e - concentration of the liquid to be treated.

This phenomenon can be reduced to a minimum by a circulation flow across the upstream surface of the membrane, which leads to the limitation of the layer thickness at the border and facilitates the reverse diffusion of rejected solutions.

3.3. Reducing the ammonium concentration using reverse osmosis

In all studies on the reduction of ammonium in water, using membrane filtration technology, good results were obtained only for reverse osmosis. Using reverse osmosis filtration technology, ammonium has been retained in over 90% of the water to be treated [16].

4. Chemical oxidation

The process of chemical oxidation has important roles in water treatment for drinking purposes, because chemical oxidants are used to oxidize or reduce inorganic compounds such as iron, manganese, ammonium or to remove the taste and odor caused by various compounds. In some cases, oxidants are also used to improve coagulation processes or to increase their efficiency [12]. Chlorine is the only oxidant which reacts with ammonium.

4.1. Chlorine - the reaction of chlorine with ammonium

Chlorine is the most common oxidizing agent used in water disinfection, but can not be used directly in gaseous form, it must first be dissolved in water. It reacts according to the following reactions:



The following figure shows that the equilibrium in the second equation is pH dependent.

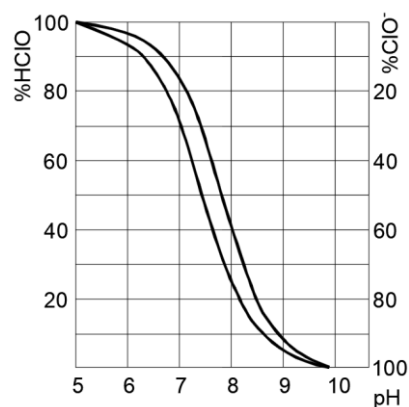
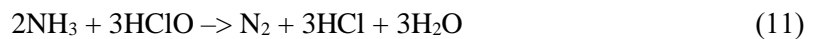
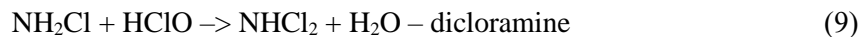


Figure 4. The dissociation of HClO in water [1].

For example: at a pH equal to 2, chlorine is in its molecular form, at a pH equal to 5 molecular chlorine disappears and all the chlorine is in the form of HClO, and at a pH above 10, all the chlorine is in the form of hypochlorous ClO^- ion [1]. In the figure above it can be seen how to calculate the quantity

of chlorine present in the form of HClO for a pH level between 5 and 10 and a given dose of free chlorine measured in water. Chlorine has a significant residual effect and its bactericidal effect is maximum when it is in the form of HClO [1].

Chlorine reacts with compounds containing ammonium or ammonia according to the following reactions [17]:



If the doses of chlorine introduced in recipients containing the same water are higher and higher, and at the end of a contact time (for example 30 min.) the concentration of residual chlorine in each container is measured, it is obtained the chlorination curve from the next figure [1].

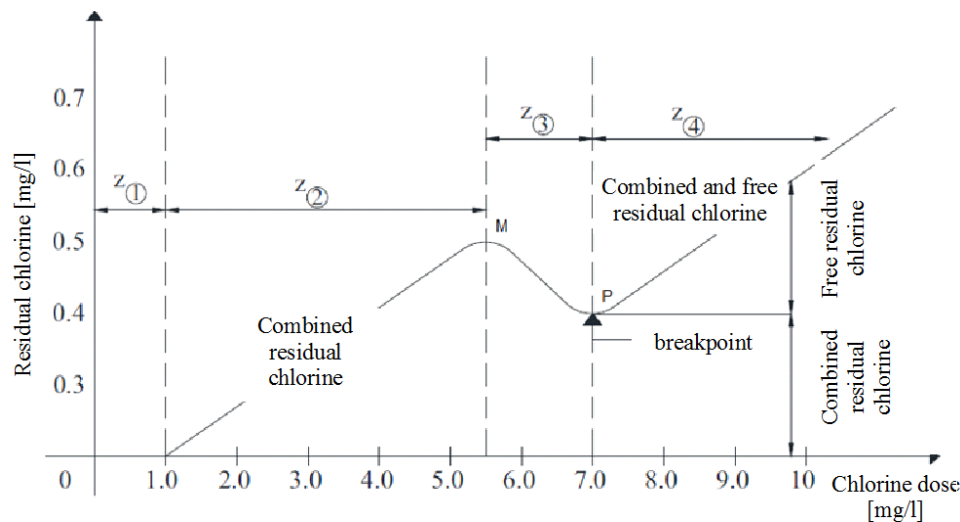


Figure 5.The chlorination curve [18].

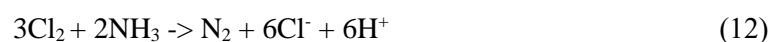
From the beginning of the curve to the M point, mono and dichloramines are formed. Beyond the M point, the added chlorine reacts with mono and dichloramines to form trichloramines and finally molecular nitrogen. After the P point (break-point) the added chlorine will have a residual effect [1], [19].

Beyond the breakpoint, the amount of residual chlorine increases in the same proportion as the amount of chlorine added. Residual chlorine is found in the form of free chlorine [1], [19].

The sum of the concentrations of the three forms of chloramine is commonly called combined chlorine and is often expressed in mg/l of Cl₂. The sum of the combined and free chlorine concentrations is called total chlorine [12].

The kinetics of the reaction of chlorine with a water containing ammonium and the formation of by-products depends on several parameters, including pH, temperature and the form in which ammonia nitrogen is found [1], [17].

4.1.1. Determination of the dose of chlorine required for the oxidation of ammonium. The required dose of chlorine, which leads to the total oxidation of ammoniacal nitrogen, is determined from the following reaction:



This reaction involves a stoichiometric dose of 7.6 g of Cl_2 for every g of N-NH_3 , which corresponds to the rupture point called the breakpoint [18].

The need for chlorine is the amount of chlorine that will react with the reducing compounds in the water, including ammonium. There is a difference between the amount of chlorine added to water and the amount of chlorine measured in water, because chlorine added to water is consumed by ammonium and other reducing compounds [18], [19].

In general, in the case of ammonium the breakpoint is displaced from the stoichiometric point of 7.6/1 and therefore the chlorination curve is determined experimentally as follows:

- Analyzes of raw water quality are made;
- The stoichiometric dose of chlorine required for the oxidation of each reducing compound in water is determined;
- 8-10 doses of chlorine different from the stoichiometric range previously determined are chosen and introduced in 8-10 water samples;
- It is agitated and leave for 30 minutes to reach the contact time;
- Samples are taken from each sample and chlorine and ammonia nitrogen concentration are determined;
- The necessary chlorine will be the dose of chlorine that will lead to a minimum concentration of ammonium and chlorine found in water.

The following figure shows an experimentally determined chlorination curve for a water sample with ammonium content [18].

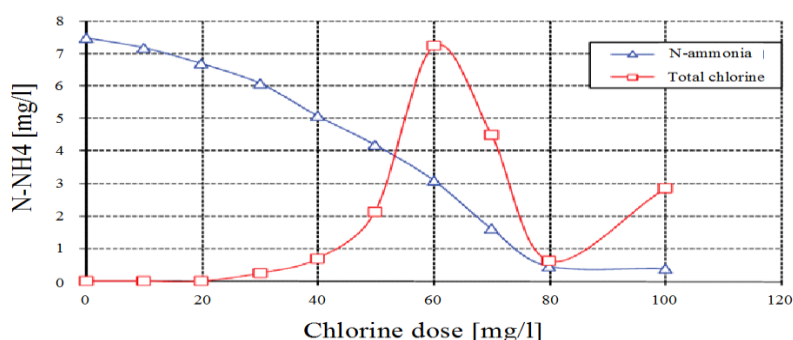


Figure 6. Chlorination curve determined experimentally for water with high ammonium concentration [18].

5. Ion exchange

Ion exchangers are insoluble granular substances which have in their molecular structure acidic or basic functions that can be changed, without any apparent change in physical appearance and without deterioration or solubilization, with positive or negative ions from water. This process, known as ion exchange, allows the ionic composition of the liquid treated to be exchanged, without changing the total number of ions in the liquid existing before the exchange [1].

By using ion exchangers with resins or by adsorption on hydrated metal oxides, cations (calcium, magnesium and barium) and anions (nitrates and anionic uranium complexes) in water can be reduced. [12].

Ion exchange and adsorption on activated aluminum oxide are treatment processes in which the adsorbent, a presaturated ion in the solid phase, is changed to an unwanted ion in the water. To achieve this reaction, a bed of ion exchange resin or aluminum oxide granules is used. The water is continuously passed through the bed, in an ascending or descending flow until in the effluent is recorded a concentration that exceeds the maximum allowable concentration for the contaminant to be reduced.

The most commonly used ion exchange reactions are reversible. In the simplest cases, the exhausted bed is regenerated using an excess of presaturated ions and ideally during the exhaustion/regeneration cycles of the materials used, no structural changes take place [12].

Natural zeolites (crystalline aluminosilicates) were the first ion exchangers used to soften water. Subsequently, zeolites were completely replaced with synthetic resins due to their faster exchange rates, longer life and much higher treatment capacity. Except the softening, the use of ion exchangers to reduce specific compounds in water has been limited due to very high costs [1].

There are 2 types of ion exchange resins and they are gel type and macroporous or weakly crosslinked type. Both resins are obtained by copolymerization, have an approximately identical structure, the only difference between them being given by porosity and the higher the crosslinking degree, the greater their mechanical resistance to both physical and chemical pressure [1] [19].

Gel resins have a microporous structure and a natural porosity resulting from the polymerization process which is limited by intermolecular distances [1].

Macroporous resins have an additional artificial porosity obtained by adding a substance. These resins have larger channels called macropores with a higher capacity for absorption and desorption of organic substances [1].

The chemical structure of ion exchangers is such that there are one or more radicals in their molecule that are either acidic or basic [1].

An ion exchange resin consists of a crosslinked polymer matrix (the usual matrix is polystyrene), to which the functional groups are covalently linked. Common functional groups splits into four categories: strongly acidic, weakly acidic, strongly basic and weakly basic. The following figure shows a three-dimensional schematic sphere made of several polystyrene polymer chains, held together by crossing with divinylbenzene [1].

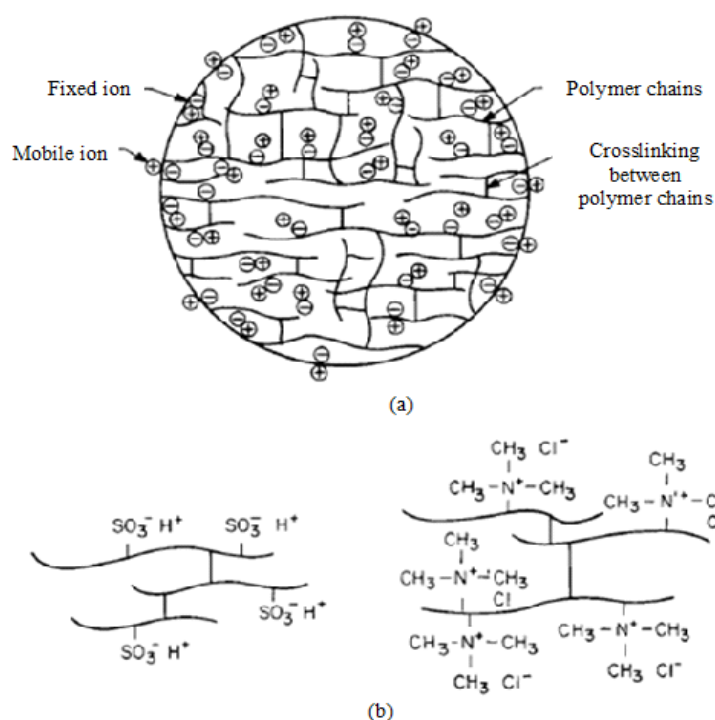


Figure 7. Ion exchange resin [2]

Negatively charged ion exchange places (SO_3^-) or (COO^-) are fixed to the resin spine or matrix. The negatively charged ion exchange places (SO_3^-) or (COO^-) are fixed to the spine of the resin or to the matrix. Positively charged mobile positions are associated by electrostatic attraction with each negative ion exchange site. The change capacity of the resin is measured as the number of fixed loading places per unit volume or per weight of the resin. Functionality is the term used to identify the chemical composition of the fixed load site, for example sulfonate (SO_3^-) or carboxylate (COO^-). Porosity (e.g.,

microporous, gel, or macroporous) is the characterization of the resin by reference to the degree of opening of the polymer structure. [1].

5.1. Ion exchange reactions

5.1.1. *Use a reversible softening reaction.* As in the case of any chemical equilibrium, it is governed by the law of mass action, whose reverse reaction corresponds to the regeneration of the exchanger.



If the liquid to be treated is brought into static contact with the ion exchanger, the reaction stops when an equilibrium is reached between the liquid and the exchanger, therefore, in order to achieve a substantial complete exchange, it is necessary to perform some equilibrium steps. by introducing water through superimposed layers [1].

The law governing reversible ion exchanges involving two A and B ions is shown graphically in the following figure [1].

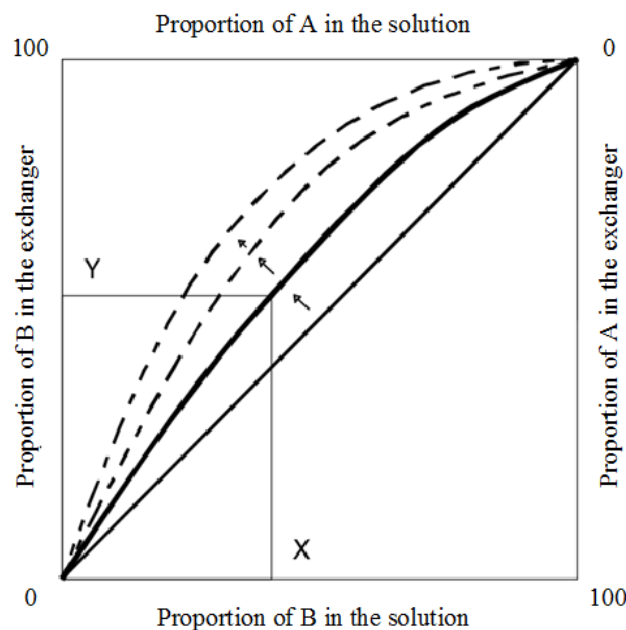


Figure 8. Ion exchange curve [1].

Under equilibrium conditions and for a B concentration of x% in solution, the ion exchanger becomes saturated up to a concentration of y%. When the two ions A and B have the same affinity for the exchange material, the equilibrium curve corresponds to the diagonal of the square. To pronounce even more, the preference of the exchange material for the B ion, the curve moves further in the direction of the arrows. The shape of the curve for a given ion system depends on several parameters: the nature and valence of the ions, the concentration of ions in the liquid and the type of exchange material [1].

As previously mentioned, the static treatment in stages, performed by introducing water in overlapping layers, the ion exchange occurs up to a certain point of the curve and then remains there [1].

If the process is to be continued until the ion is effectively reduced in favor of another ion, the equilibrium point must be gradually changed by passing the liquid through a series of successive layers, which contain ions which must be retained less and less, until it moves along the equilibrium curve close to the zero concentration point for the ion to be removed [1].

5.1.2. Use of an irreversible reaction. This reaction is used to reduce a strong acid by a strong base anion exchanger:



The reverse reaction is practically non-existent, the exchange being complete, it can be obtained just as well in static or percolary contact conditions. In this case the ion leakage can be equal to 0, provided that the contact time between water and resin is long enough [1].

Equilibrium reactions that give rise to an insoluble composition can be compared to this type of exchange. For example, if seawater is treated with an ion exchanger saturated with silver ions, the following reaction is obtained:



because AgCl is insoluble, it precipitates.

Under these conditions, the balance changes completely and the reaction is complete, even in static conditions. Ion exchange is not instantaneous, and the reaction rate depends on the type of resin [1].

The two types of reactions mentioned above can be used for:

- to reduce one or more unwanted ions in the liquid to be treated;
- selection and concentration in the ion exchanger of one or more ions that will be bound later in the purified state and concentrated in the regeneration liquid [1].

5.1.3. Use of a previously attached anionic complex. This ionic complex is likely to cause secondary effects, such as oxidation-reduction phenomena that affect the ions in the water or the liquid to be treated, without dissolving in the liquid [1].

5.2. Regeneration methods

At the end of each ion exchange cycle it is necessary to regenerate the ion exchanger.

Regeneration is done by introducing a concentrated solution with A ions, in the ion exchanger, which flows in the same direction as exhaustion (co-current regeneration) or in the opposite direction to exhaustion (countercurrent regeneration) [1].

5.2.1. Co-current regeneration. Consists in bringing the concentrated solution with A ions in contact with those upper layers of the exchanger, saturated with B ions, which are then removed from the resin and brought into contact with those layers which are not so exhausted and which ensure conditions optimal to capture B ions. Therefore, it seems that in order to obtain a total regeneration, it is necessary that an amount of ions corresponding to the A/B ratio undergo a double exchange process [1].

If the amount of regeneration solution is limited, the B ions cannot be completely removed from the exchangers, and the lower layers of the exchanger are not completely regenerated. Consequently, during the next cycle, the B ions will undergo self-regeneration by the A ions in the upper layers [1].

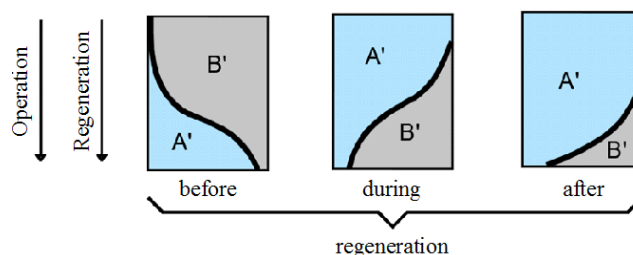


Figure 9. Co-curent regeneration [1].

5.2.2. Countercurrent regeneration. Consists in bringing the concentrated solution with A ions in contact with the lower layers of the exchanger (because the flow is made from the bottom up), which

are not saturated with B ions, which in favorable conditions are eliminated and can no longer be recovered. in the exhausted upper layers [1].

Therefore regeneration is more reversible and more efficient than co-current regeneration [1].

The main advantages of countercurrent regeneration:

- has a high efficiency and requires fewer reagents
- good quality water results because the lower layers are regenerated more efficiently.

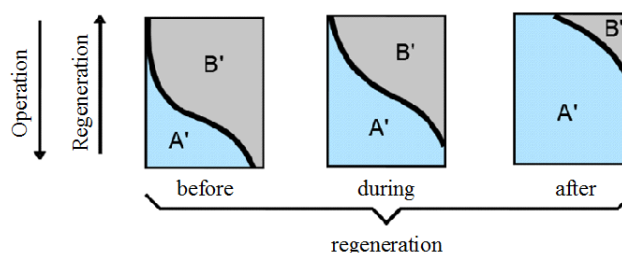


Figure 10. Countercurrent regeneration [1].

5.3. Ion exchange characteristics

The main features of an ion exchanger are the following:

- The exchange capacity of an ion exchanger - represents the amount of ions that can be retained per unit volume of the exchanger;
- Bed volume - represents the volume of liquid to be treated per hour/volume of resin;
- Ion flow - represents the bed volume x water salinity;
- Regeneration level - represents the weight of the reagent used / the volume of the ion exchange material;
- Regeneration ratio - (gram-equivalent of regeneration reagent / gram-equivalent of reduced ions) x 100;
- Regeneration efficiency - represents the opposite of the regeneration ratio;
- Ion leakage - represents the concentration of unwanted ions left in the treated liquid;
- Penetration - represents the maximum allowable ion leakage until the end of the production cycle;
- Degree of wear - represents the mechanical wear of the exchanger during operation.

5.4. Reducing the ammonium concentration using ion exchangers

Numerous studies conducted to reduce ammonium in water using ion exchange have led to the following conclusions [7]:

- The ammonia retention capacity with different adsorbents increases with the increase of the initial ammonium concentration and with the increase of the quantities of adsorbents;
- The rate of ammonium reduction was initially fast, then gradually decreased, with a longer contact time;
- Particle size, pH, competing ions and their concentrations can affect ammonium retention;
- Ammonium adsorption was spontaneous and exothermic;
- The presence of fatty acids can affect the efficiency of ammonium removal.

6. Air stripping

Air stripping is the transfer of volatile components of a liquid into an air flow. Volatile compounds have a relatively high vapor pressure and a low solubility in water, characterized by the coefficient of Henry's law, which represents the distribution or equilibrium repartition of an organic contaminant between air and water [12], [20].

$$K_{eq} = \{A\}_{air} / \{A\}_{water} \quad (16)$$

K_{eq} = equilibrium constant;

$\{A\}_{air}$ = activity of component A in the gas phase;

$\{A\}_{water}$ = the activity of component A in the aqueous phase.

At an atmospheric pressure, the gas behaves ideally, and the above equation can be reduced to:

$$H = K_{eq} = P_A / \delta_A A \quad (17)$$

H = Henry's constant [atm-L/mol] of component A;

P_A = pressure A exerted in the gas phase [atm];

δ_A = activity of A in the aqueous phase;

[A] = molar concentration of A in the aqueous phase [mol/l].

The presence of air does not affect Henry's law constant for organic substances or gases, because the components of air have a very low solubility in water.) For very low concentrations, Henry's law can be written as follows:

$$P_A = H[A] \quad (18)$$

When organic or inorganic species dissolved in water do not affect the balance of distribution/repartition, the equation $P_A = H[A]$ is generally valid for concentrations lower than 0.01 gmol/L, but in practice, the equation was valid for concentrations higher than 0.1 gmol/L [12].

When Henry's constant for a compound of interest is not available, it can be determined if the water solubility and the vapor pressure component are known.

The main factors that influence the distribution of the balance between air and water are represented by temperature, ionic concentration, pH and surfactants. The balance is not affected by the total pressure because most aeration and stripping devices operate at atmospheric pressure [12].

For temperatures encountered in water treatment, H tends to increase with increasing temperature, as the aqueous solubility of the component decreases as the vapor pressure increases. The value of H at a temperature of 20°C, in the case of ammonium, is 0.000574 [12].

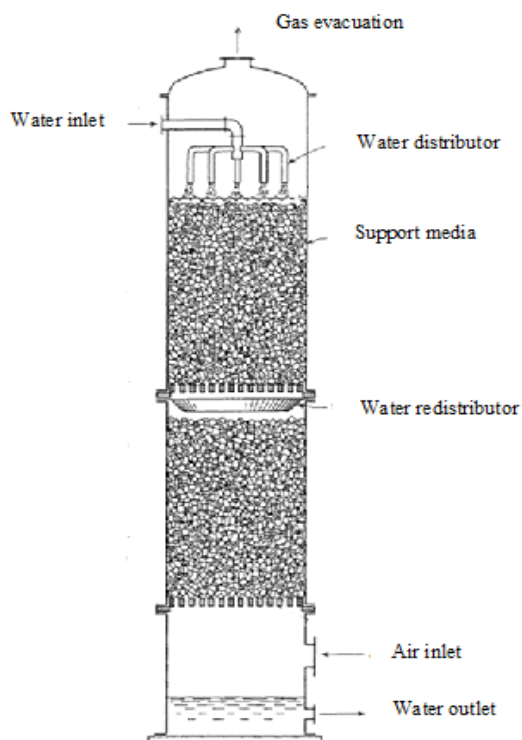
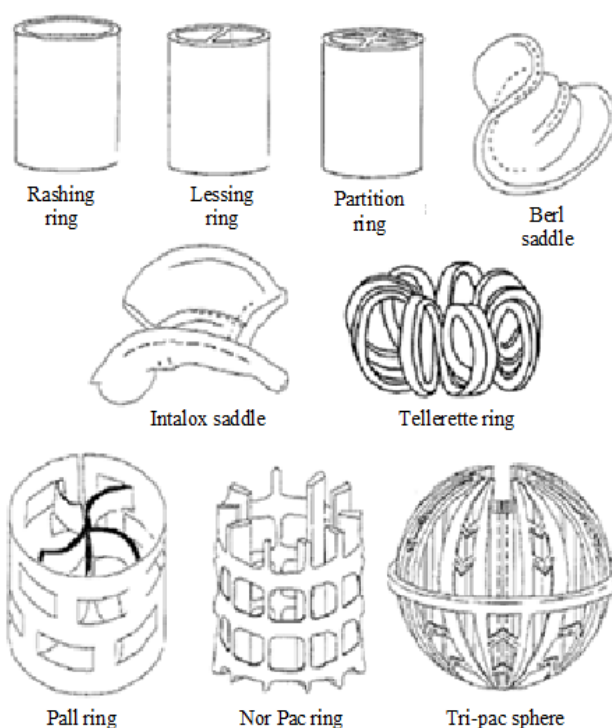
For most water supply systems, the ionic resistance is less than 10 mM and the activity coefficient is equal to 1. The significant increase in volatility and apparent constant of Henry are observed only for waters with a strong ionic resistance, such as sea water [12].

pH does not affect Henry's constant itself, but it does affect the distribution of species between ionized and non-ionized forms. This, in turn, influences the global gas-liquid distribution of the compound, because only non-ionized species are volatile. At neutral pH, ammonia is present as an ammonium ion and cannot be stripped, but if the pH of the water rises above 10, the ammonia is not an ion and can be stripped [12].

Several types of air stripping systems are widely used for a variety of water treatment applications, including reducing ammonium in water. Water treatment applications for these systems include gas absorption for stabilization and disinfection, precipitation of inorganic compounds, air stripping of volatile inorganic compounds and harmful dissolved gases. [12].

6.1. Towers with support media (Packed towers)

The primary applications of towers with support media in water treatment are the stripping of volatile organic compounds, carbon dioxide, hydrogen sulfide and ammonia. The following figure 11 shows a tower with support media, where water is pumped to the top of the tower, is evenly distributed and flows gravitationally through the support environment. At the same time, air is introduced at the bottom of the tower. [12].

**Figure 11.** Tower with support media [12]**Figure 12.** Support media [12], [20].

The support environment ensures a very large contact area between air and water, which leads to the efficient transfer of volatile compounds from water to air. Air-stripped water reaches the bottom of the tower, and contaminants reach the top of the filter, where they are collected for neutralization, or released into the atmosphere if they do not represent a risk to the environment. [12].

Cross-flow, cascade and co-current tower systems with support media have similar configurations, but the air flow is introduced differently. In the cross-flow system, air flows over the tower support medium at an angle of 90° to the direction of water flow. In the cascade flow system, air is introduced at various points along the tower and flows countercurrently with the water flow [12].

Both cross flow and cascade flow systems provide higher airflow rates than those commonly used in conventional countercurrent systems. Higher air rates will provide greater force for stripping, leading to a more efficient reduction of contaminants with low volatility. Cross-flow and cascade systems are recommended when high air-water ratios are required to remove semi-volatile, low-solubility contaminants from water.

In the co-current system, both air and water enter the top of the tower, flow through the support medium and are discharged to the bottom of the tower. The co-current system is rarely used in water treatment [12].

Columns made from the sieves have recently been used to remove volatile compounds from water. The columns made from the sieves work as a countercurrent process. The columns are usually less than 10 m high and consist of several sieves, placed in series along the column. [12].

Usually high air flows are used, causing very small bubbles or foam to come in contact with air and water. The foaming ensures a large water-air contact surface, necessary for the mass transfer. The increase of the removal efficiency is obtained by increasing the surface of the sieves. The advantages of using such a sieve tower, instead of a classic one, are: this tower is much more compact and the maintenance work is much easier.

The main disadvantage is that high air flows rates are required, which leads to a higher operating cost [12].

6.2. Reducing the ammonium concentration using air stripping

Air stripping is less used in drinking water treatment, it is used in industry, in distillation towers. In distillation towers, the steam used has 2 purposes: heating the water and reducing the concentration of dissolved gases.

The implementation of this type of installation requires special precautions both in terms of equipment selection and in terms of operation [1].

7. Summary of the advantages and disadvantages of current ammonium reduction technologies

The following table summarizes the advantages and disadvantages of the technologies used to reduce ammonium in water.

Table 1. Ammonium reduction technologies - Advantages / Disadvantages.

Item	Process	Advantages	Disadvantages
1.	Biological processes	<ul style="list-style-type: none"> Relatively low costs; Without consumption of chemical reagents. 	<ul style="list-style-type: none"> process dependent of temperature, alkalinity, pH, dissolved oxygen nitrite formation is possible; slow process priming; requires additional source of carbon in the case of water with low alkalinity; biomass management is complicated; requires GAC adsorption. [13], [21]
2.	Reverse osmosis	<ul style="list-style-type: none"> high efficiency; simple operation. 	<ul style="list-style-type: none"> requires water pretreatment; requires automatization; high cost if all the water flow passes through the installation; requires remineralization; the concentrate (30% of the treated flow) is difficult to manage. [16]
3.	Break-point chlorination	<ul style="list-style-type: none"> high efficiency; relatively low cost; other pollutants are also oxidized (iron, manganese, nitrites); relatively short reaction time (30 min.). 	<ul style="list-style-type: none"> high doses of chlorine are required; it is possible to form trihalomethanes; nitrite formation is possible; requires automatization; requires GAC adsorption. [22], [23]
4.	Ion exchangers	<ul style="list-style-type: none"> high efficiency; simple operation. 	<ul style="list-style-type: none"> Water pretreatment is necessary requires automatization; high costs in case of water with high mineralization; requires reagents for regeneration; the solution from regeneration is difficult to manage; [7], [24], [25]
5.	Air stripping	<ul style="list-style-type: none"> used in industry 	<ul style="list-style-type: none"> difficult operation; requires special equipment [26]

8. General conclusions

The article presented the technologies and processes currently available for reducing ammonium in water. These are briefly described below.

Biological processes - biological processes have a high efficiency in reducing ammonium, but are very expensive, difficult to operate and require special conditions for the development of microorganisms. Due to the risks associated with the biological process, its application should be done only after pilot scale tests to show if the water can be treated by nitrification processes and if the entire amount of ammonium is converted into nitrates.

Reverse Osmosis - Reverse Osmosis is an effective ammonia reduction technology, as it reduces the concentration of ammonium in the water by over 90% and is very easy to operate without the need for qualified personnel. This technology is limited by the very high energy consumption required to pump water through the membrane.

Breakpoint chlorination - is the most widely used method of reducing ammonium in water, as chlorine is the only oxidizing agent eligible for reducing ammonium in water. This method requires high doses of chlorine and requires automation of the dosing system.

Ion exchangers - In the case of waters with high mineralization in which the concentration of calcium and magnesium is high and the concentration of ammonium is relatively low, the ion exchange leads to high costs due to the frequent regeneration of cationite. In addition, the solution resulting from regeneration that contains high concentrations of salt and ammonium is a waste that can create complications in management (can not be accepted in the waste water treatment plant).

Air stripping - the technology is efficient in industry, in drinking water treatment it is less used, but it is limited by the fact that it requires special equipment and that it requires qualified personnel, the operation being difficult.

The most used technologies for reducing ammonium in water are the technologies that use biological processes, reverse osmosis and breakpoint chlorination, and their efficiencies in reducing ammonium are 80-90% for biological processes, 60-90% for reverse osmosis and 80-95 % for breakpoint chlorination.

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