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DOCTORAL THESIS

**Treatment processes for ammonia reduction in
drinking water**

SUMMARY

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1. Introduction

1.1 General data

Nitrogen is an essential nutrient for plants and animals, and is a key element for proteins and cells [1]. Nitrogen is the most abundant element in the Earth's atmosphere, being present in a proportion of 79% of the total gases. The atmosphere is practically an inexhaustible reservoir of nitrogen gas, but nitrogen cannot be assimilated directly by plants unless it is combined with hydrogen or oxygen [2], after that the plants can be consumed by animals.

In living organisms, nitrogen is found in amino acids, in proteins, in nucleic acids (DNA and RNA) and in the energy transfer molecule, adenosine triphosphate [3].

The first industrial and agricultural applications of nitrogen were in the form of sodium nitrate or potassium nitrate.

1.2 Nitrogen circuit in nature

The nitrogen circuit is the biogeochemical cycle by which nitrogen is transformed into multiple chemical forms as it circulates through atmospheric, terrestrial and marine ecosystems. Nitrogen conversion can be realised through both biological and physical processes.

The major transformations of nitrogen are: fixation, nitrification, ammonification, assimilation and denitrification [4].

The transformation of nitrogen into its many oxidizing states is the productivity key in biosphere and is highly dependent on the activities of a diverse set of microorganisms, such as bacteria and fungi [4].

1.3 The impact of human activities on the nitrogen circuit

The human impact on the nitrogen circuit in nature is represented by intensive agriculture and industrial development. In the last century, the global nitrogen circuit has been significantly altered due to anthropogenic nitrogen sources.

From year to year there are more and more human activities that have a significant impact on the nitrogen circuit in nature. Burning fossil fuels, applying nitrogen-based fertilizers and other activities can dramatically increase the amount of biologically available nitrogen in an ecosystem.

1.4 Forms of nitrogen in water

In groundwater and surface water sources, nitrogen is found in several forms, taking into account its nature and oxidation state (at the time of determination). By its nature, nitrogen can be dissolved or in other forms: colloidal and/or free. In dissolved form, nitrogen can be in the form of mineral nitrogen and organic nitrogen [5].

The following table shows the forms of mineral nitrogen dissolved in water, as well as the chemical expression and oxidation state in which they are found.

Table 1.1. Forms of mineral nitrogen dissolved in water, chemical form and oxidation state [2].

Nr.	Nitrogen form	Chemical formula	Oxidation state
1	Ammonia	NH ₃	-3
2	Ammonium ion	NH ₄ ⁺	-3
3	Nitrogen gas	N ₂	0
4	Nitrite ion	NO ₂ ⁻	+3
5	Nitrate ion	NO ₃ ⁻	+5

Nitrogen concentrations in water sources are generally low, but can reach very high concentrations due to infiltration from agricultural areas, infiltration from non-compliant landfills or untreated or insufficiently treated wastewater discharges.

Nitrogen from domestic wastewater is made up of 60-70% ammonium and 30-40% organic nitrogen, which means that ammonium is an important source of pollution, and it increases as the concentration of total nitrogen in domestic wastewater discharged in water sources increases.

1.5 Ammonium

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].

Natural ammonium concentrations in surface and groundwater sources are low. The presence of higher ammonium concentrations than geogenic in surface water sources is an important indicator of water pollution [7].

Ammonium itself has no toxic effects on human or animal health and would not limit the use of water, its sanitary importance consists in the fact that it indicates the water pollution with other chemical or especially bacteriological elements that can have harmful effects on human health.

Ammonium concentrations in non-degraded natural water sources are usually low, but ammonium concentrations from intensive agriculture, industrial and other human activities have a negative impact on water sources.

In the drinking water treatment plants, the excess ammonium concentrations are undesirable because the presence of excess ammonium in water leads to an increase in the chlorine consumption used in disinfection and thus to a reduction of the efficiency in the disinfection stage of the treatment plant. Ammonium can interfere with manganese removal filters, as oxygen would be used largely for ammonium nitrification, resulting in an earthy taste [7].

Its presence in the distribution networks leads to the bacteria development on the pipes walls of which the distribution network is composed and to the oxidation of ammonium to nitrites and nitrates, toxic compounds that have negative effects on human health.

1.6 Current legislation regarding ammonium

Water is an indispensable component of life, environment and of society development. Sustainable development depends on the water sources management, water being a vulnerable and

limited resource. As water is a limited resource globally, it is necessary to manage existing water sources, to ensure water resources for future generations [8].

Water is not a commercial product, it is a common good and a limited resource that must be protected and used in a sustainable way, both qualitatively and quantitatively [9].

In Romania, the maximum allowable limit for ammonium in drinking water, according to Law 458/2002 is 0.50 mg/l [10]. Law 458/2002 on drinking water quality in Romania, represent the transposition of Directive 98/83/EC (reformed by Directive 2184/2020 / EC).

In countries where there are no drinking water laws and standards, there are usually targets to be achieved for drinking water quality parameters, and these targets are usually taken as the World Health Organization's stability guide values.

According to the World Health Organization, ammonium is found in drinking water at concentrations below those that have an impact on human health, but concentrations that impact water quality on taste (35 mg/l) and odor (1.5 mg/l) are specified [11].

2. Water sources with high ammonium concentrations

2.1 Sources of contamination with ammonium

Concentrations in non-degraded natural water sources are usually low. In reality, intensive agriculture, infiltration, domestic and industrial effluents, contribute substantially to ammonium pollution of surface and groundwater sources. Sources of pollution can be direct such as: domestic and industrial wastewater, animal manure, leachate and infiltrations from landfills or indirect such as nitrogen fixation, infiltrations from agricultural land, construction sites and atmospheric deposits [12] [13].

Ammonium concentrations in surface water sources vary seasonally and regionally and are affected by anthropogenic activities. Ammonium concentrations in surface water vary seasonally, being higher in winter and spring and lower in summer and autumn.

Ammonium concentrations in rivers and lakes are usually lower than 6 mg/l, and at higher concentrations, they may indicate a source of anthropogenic pollution [14].

Natural concentrations of ammonium in groundwater sources are usually below 0.2 mg/l, and higher concentrations of up to 3 mg/l are found in forested areas and in layers rich in humic substances and iron [7].

Due to ammonium pollution of water sources, ammonium concentrations in groundwater have increased considerably from year to year and contain higher ammonium concentrations than surface water sources.

2.2 Water sources with high ammonium concentration in Romania

In Romania the available water sources are represented by underground sources (wells, springs) and surface sources (rivers, lakes, Danube river and Black Sea).

According to some records from 2009, on the rivers where registered ammonium concentrations were above the maximum admissible limit according to Law 458/2002, there are generally industrial pollutants or communal households that do not benefit of centralized sewer networks and wastewater treatment systems.

The following figure shows the classification of Romanian lakes in the trophicity categories, depending on the nutrients values in water, in 2009.

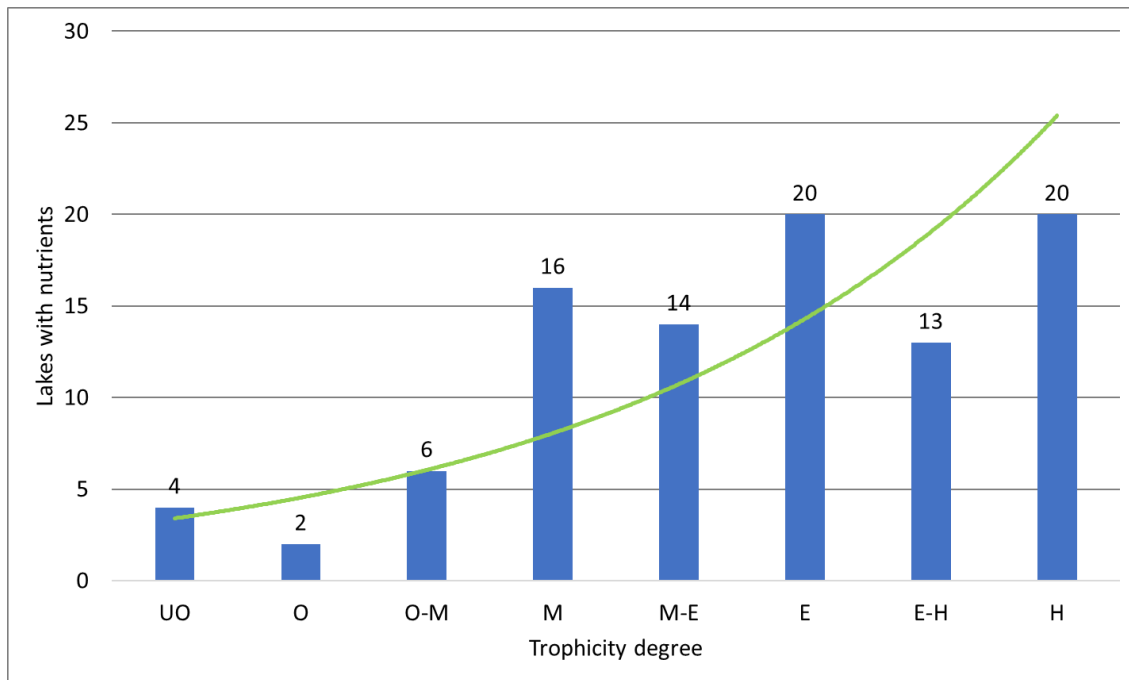


Figure 2.1. The trophicity degree of the Romanian lakes depending on the nutrient concentrations in 2009 [8].

As can be seen in the above graph, the nutrient concentrations in the Romanian lakes are very high, which reflects a large number of lakes that have a high trophicity. This high trophicity indicates degradation of water quality and affects the lakes biodiversity.

The following figure shows the variation of ammonium contamination of Romanian groundwater bodies, in the period 2012-2017.

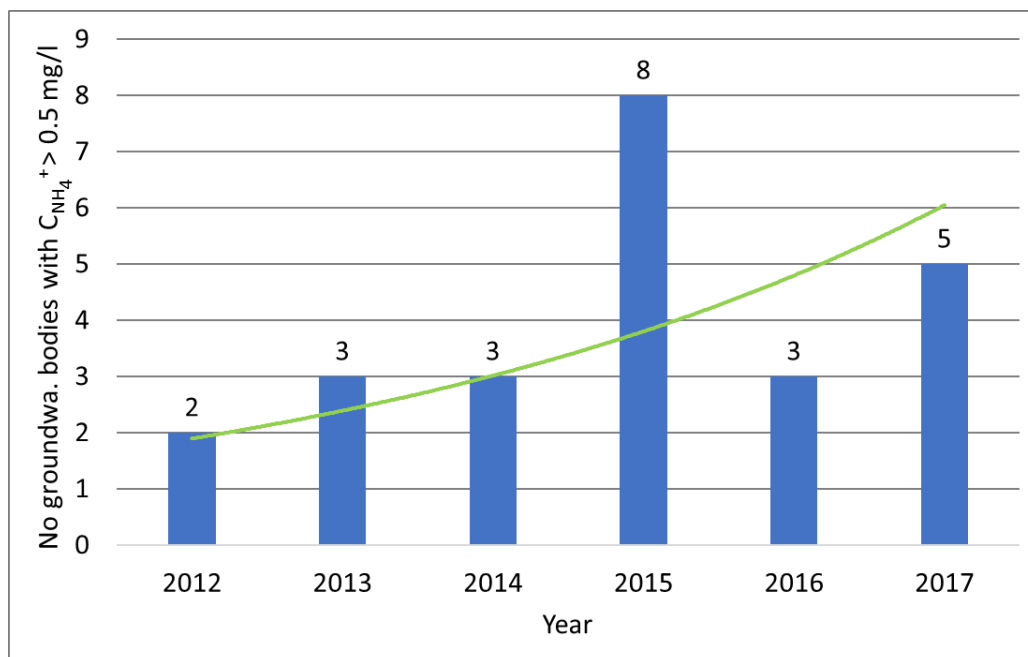


Figure 2.2. Variation of ammonium contamination of Romania groundwater sources [15] [16] [17] [18] [19].

As can be seen in the above graph, the trend of ammonium contamination of groundwater sources in Romania is increasing. This tendency to increase the ammonium concentrations in water leads to a degradation of the raw water quality and implicitly to the need for ammonia removal technologies, which ultimately leads to an increase in the tariff of water supplied to consumers.

2.3 Water sources with high ammonium concentration in other countries

Ammonium contamination of water sources is a global phenomenon, as in all countries there are human activities that lead to pollution of either groundwater or surface water sources.

Ammonium contamination of rivers in the Member States of the European Union, according to the maximum ammonium concentration recorded between 2001-2011, is very high, in over 90% of rivers there were exceedances of ammonium concentrations above the maximum allowable limit of 0.5 mg/l according to Law 458/2002 and in over 45% of cases ammonium concentrations exceeding 5 mg/l were recorded.

3. Current state of the existing technologies that treat water with high ammonium concentration

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 [20].

Although there are various technologies for removing ammonium from water, they are limited. The limitations of current technologies are due to high operating costs, low ammonia reduction/oxidation rate, high sensitivity to pH, temperature and various elements in water [20].

3.1 Biological processes

Biological processes used in the reduction of nitrogen-based compounds in water [21] can be divided into:

- Nitrification - The first process involves the ammonium concentration reducing in water by oxidizing it to nitrate. This process is realised by specific bacteria, which sequentially oxidize ammonium to nitrate with an intermediate form of nitrite;
- Denitrification - The second process involves reducing the nitrate concentration in water by oxidizing it to nitrogen gas. Unlike nitrification, this process is performed by different species of bacteria.

3.1.1 Nitrification

Nitrification is the biological process of oxidizing ammonium to nitrate with an intermediate form of nitrite. Nitrification is usually realised by *Nitrosomonas* and *Nitrobacter*. Both species of bacteria are classified as autotrophic organisms [5].

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* [2] [5].

For the nitrification process to work optimally, it is recommended that the minimum level of dissolved oxygen concentration be 2 mg/l [5].

The theoretical ratio between alkalinity and oxidized ammonium is 7.1 mg CaCO₃/mg oxidized ammonium. In open systems that use air as a source of oxygen, the alkalinity reduction ratio is generally equal to or less than the theoretical level [2].

For the nitrification process to work optimally, it is recommended that the pH be maintained in the range of 6.5-8, with an optimal pH of 7.2 [5].

Nitrifying bacteria are susceptible to a wide range of organic and inorganic inhibitors. However, nitrifying bacteria can adapt to many inhibitory compounds when the inhibitors are constantly present in the raw water, compared to the appearance of high concentrations due to accidental discharges into the water source of untreated or insufficiently treated industrial wastewater.

3.1.2 Denitrification

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

Unlike nitrification, a relatively wide range of bacteria can achieve denitrification; including *Pseudomonas*, *Micrococcus*, *Archromobacter* și *Bacillus* [21].

Denitrification is influenced by dissolved oxygen, with a maximum optimal concentration of 0.2 mg/l for pure cultures, 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 [5].

In the denitrification process the rate of nitrate reduction is influenced by temperature. At a temperature below 20°C, the process is more influenced than at temperatures higher than 20°C [5].

Bicarbonates are produced in the denitrification process, so the process is affected by pH and alkalinity. The alkalinity produced is 3.57 mg alkalinity expressed as CaCO₃, produced per mg of nitrogen from reduced nitrate to nitrogen gas. [2].

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 [5].

Denitrifying bacteria are more sensitive to inhibitory compounds than nitrifying bacteria; the ability of biomass to acclimatize to higher concentrations of inhibitory substances is also considered [5].

3.2 Reverse osmosis

Reverse osmosis process is a physical process of filtering water through a membrane with very fine mesh and is performed at pressures above the osmotic pressure (5-8 MPa). Reverse osmosis retains practically over 95% of the elements present in water and produces an ultrapure water that needs remineralization to become potable [22].

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 [23].

Using reverse osmosis filtration technology to reduce the ammonium concentration in water, ammonium can be retained in over 90% of the water to be treated.

3.3 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 of water treatment plant [24].

Chlorine is one of the most versatile chemicals used in water and wastewater treatment and is the only oxidant that reacts with ammonium.

Ammonium oxidation in water is realised by breakpoint chlorination. The dose of chlorine required for the ammonium oxidation is determined experimentally by performing the chlorination

curve. The chlorination curve indicates the breakpoint, and after this point, the chlorine added to the water acts as residual chlorine.

The chlorination curve can be obtained experimentally by introducing increasing doses of chlorine into containers containing the same water. After a contact time of 30 minutes, the total chlorine concentration in each container is measured and thus the breakpoint chlorination curve shown in the following figure is obtained.

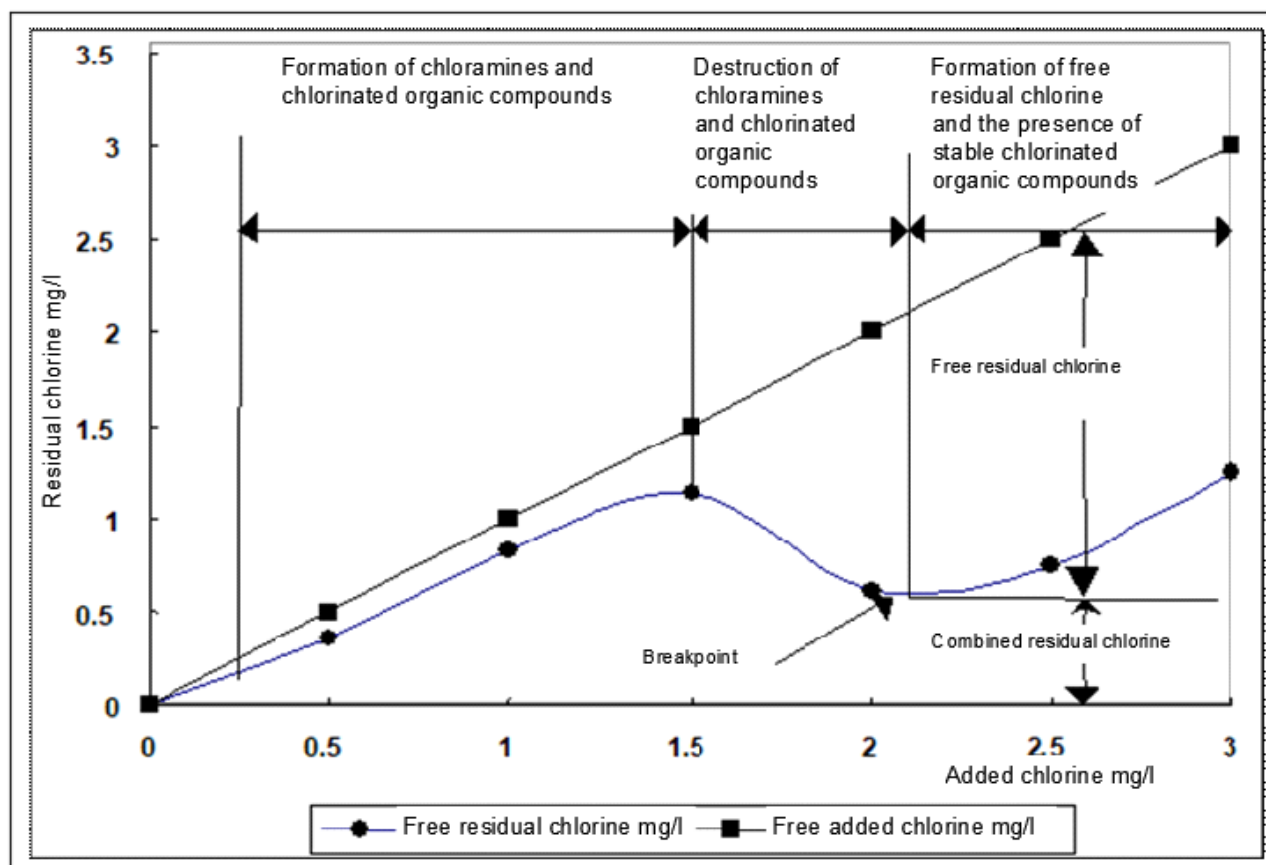


Figure 3.1. Chlorination curve [25].

3.4 Ion exchangers

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 [23].

Natural zeolites (crystalline aluminosilicates) were the first ion exchangers used to soften water.

The selectivity of natural zeolites for a given ion depends on its origin, as well as on the type of ions already present in the structure [26].

In the case of reducing the ammonium concentrations in water, there are 3 natural zeolites that are very effective in retaining ammonium ions, called clinoptilolite, modernite and mesolite, the last 2 zeolites not being very common.

With the technology development, zeolites were replaced with synthetic resins due to their faster exchange rates, longer life and much higher treatment capacity [23].

At the end of an ion exchange cycle, regeneration of the ion exchanger is necessary.

Regeneration is realised by introducing a concentrated solution with ions A, in the ion exchanger saturated with ions B, which flows in the same direction as exhaustion (regeneration in co-current) or in the opposite direction to exhaustion (regeneration in countercurrent) [23].

3.5 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 [24].

Ammonium reduction in water can be realised by bringing small drops of water into contact with a large amount of air. This physical process is called desorption, but the most commonly used name is ammonium/ammonia air stripping [21].

To remove ammonium nitrogen from water, it must be in molecular form (NH_3) and not in the form of ammonium ion (NH_4^+). This is realised by raising the water pH to 10 or 11, usually by adding lime, which leads to the conversion of ammonium ions into ammonia and reducing its concentration by stripping with air. Reducing the concentrations of ammoniacal nitrogen in water by stripping it with air has no effect on the nitrites, nitrates and organic nitrogen concentrations [21].

The main stripping systems are towers with support media and are mainly used for the NH_3 , CO_2 , H_2S and volatile organic compounds removal. Towers with support media have co-current, cascade, countercurrent, and cross-flow configurations [24].

4. Biofilters

4.1 General data

The biological processes used to reduce ammonium in water intended for human consumption are mainly processes with attached biomass. These biological processes take place in biological tanks called biofilters or biological reactors. Biofilters are characterized by the presence of microorganisms that adhere to the support media in the form of a fixed film (biofilm).

Unlike other technologies used to reduce ammonium concentrations in water, biofilters have the lowest impact on the environment and do not require high power consumption. With low environmental impact and very low operating costs, biofilters can be included in the treatment plant sustainable development.

4.2 Biofilters types

Biofilters are used for drinking water treatment, wastewater treatment (domestic and industrial), but also for air treatment.

From the point view of the operation mode and of the support media used, the biofilters used in water treatment are:

- Trickling filters, in which the support media is package type. In this type of biofilter, water flows gravitationally through the support media, in the form of a thin film, and the flow is with free surface;
- Rotating biofilters, in which the support media is disc type;
- Submerged biofilters, in which the support media is generally represented by a granular material immersed in the mass of water.

In general, biofilters used in water treatment intended for human consumption are submerged biofilters.

4.3 Biofilm

Nitrifying or denitrifying bacteria can attach to various media and grow as a dense film belonging to a viscous-gelatinous matrix. The water to be treated passes over this film in the form of thin films containing dissolved organic substances, ammonium and nitrates, substances which are assimilated by the biofilm due to the gradients of diffusion. Suspended and colloidal particles cannot penetrate the surface of the biofilm, but are decomposed on the surface into soluble substances. The oxygen in water and the air in spaces of the support media provide the necessary oxygen for the aerobic reactions on the biofilm surface. The products resulting from the metabolic processes are diffused to the outside and are transported outside the system, through the treated water [27].

4.4 Processes involved in biofilm

The critical point for the biofilter successful operation is to control and maintain the biomass in good condition on the support media surface. Because the performance of the biofilter depends on microbial activity, a constant amount of substrate (organic matter and nutrients) is required for long-term and efficient operation. In the biofilter activity there are 3 important processes, namely

microorganisms fixation, microorganisms development and the film detachment from the support [5].

4.5 Factors that influence biological filtration

In addition to the factors that affect the biological nitrification or denitrification process, the biofilter efficiency also depends on the media type used, height of the media layer, concentration of pollutants, contact time and on the media washing.

The support media is the most important factor of biofiltration, because this media represents the support for the bacteria growth. There is a wide variety of media used in biofilters and are represented by: stones, gravel, sand, plastics and synthetics, anthracite, wood, zeolites, granular activated carbon and ceramic granules.

The media used in biofilters should provide a suitable surface for rapid biomass fixation, a large surface area for biomass growth and a good surface texture to keep the biomass stable against premature detachment [28].

More recently, a new type of ceramic granule support media has been discovered that can increase and improve water production. Ceramic granules are made of high quality clay and are obtained by grinding, filtering, pouring and calcining. The product is represented by uniform granules, with a red and brown appearance. This substrate has a porous surface and strong adsorption [29].

4.6 Biofilters with submerged media

The interest in submerged biofilters has increased due to the appearance and development of plastics and other materials, which have large areas necessary for the biofilm development. These filter media have also been shown to be highly effective for nitrification [27].

Depending on the water flow through the support media, biofilters with submerged support media can be:

- With upward flow;
- With downward flow.

Biofilters with submerged media and with ascending flow, depending on the degree of expansion of the bed can be:

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

5. Description of equipment and experimental stand

5.1 *Experimental tests purpose*

In order to reduce the ammonium concentration in water, the biological nitrification process with attached biomass was used in the realised experimental determinations. In this process, the ammonium in raw water is oxidized to nitrite and finally to nitrate by nitrifying bacteria. The reduction of nitrate concentration in water was not the subject of the experimental determinations in this doctoral thesis.

The main object of the experimental tests was the determination of the biofilters efficiency in reducing the ammonium concentrations in water. Also, the influence of the ammonium concentration in raw water on the nitrification process, the influence of the contact time and the behavior of the filter layer in terms of nitrification efficiency were objectives of the experimental research.

In addition, the experimental tests aimed to determine the impact of the ammonium concentration sudden change in raw water on the biofilters efficiency in reducing its concentration in water, compared to the biofilters efficiency obtained after a period of one week, in which synthetic raw water with the same ammonium concentration were introduced in biofilters.

5.2 *Pilot installation*

The experimental tests were performed on a pilot installation, which is part of the Colentina Laboratory Complex and aimed to determine the biofilters efficiency in reducing ammonium in raw water depending on the biofilter support media/filtration media.

The following figure shows the technological scheme of the biofilters pilot installation.

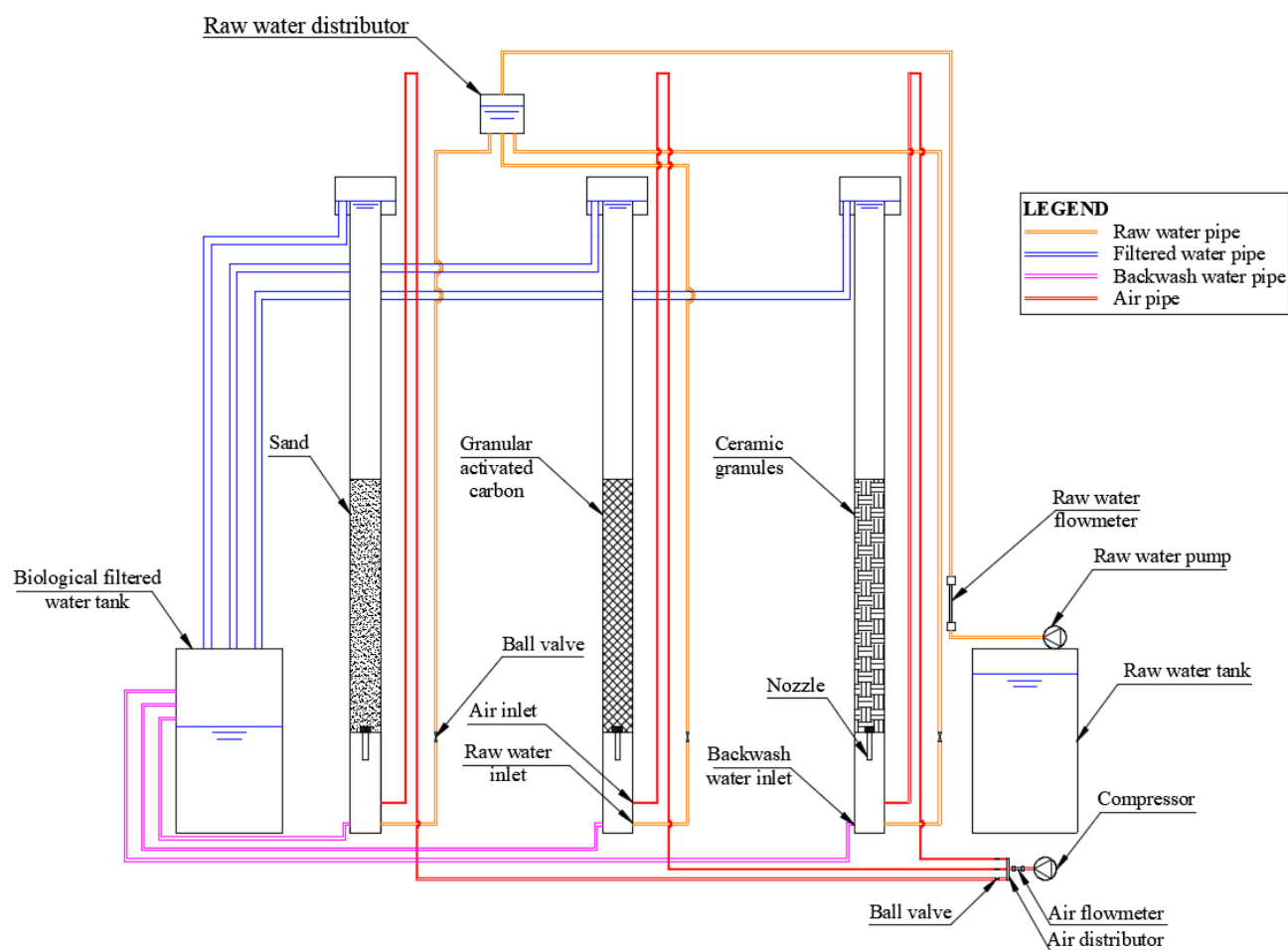


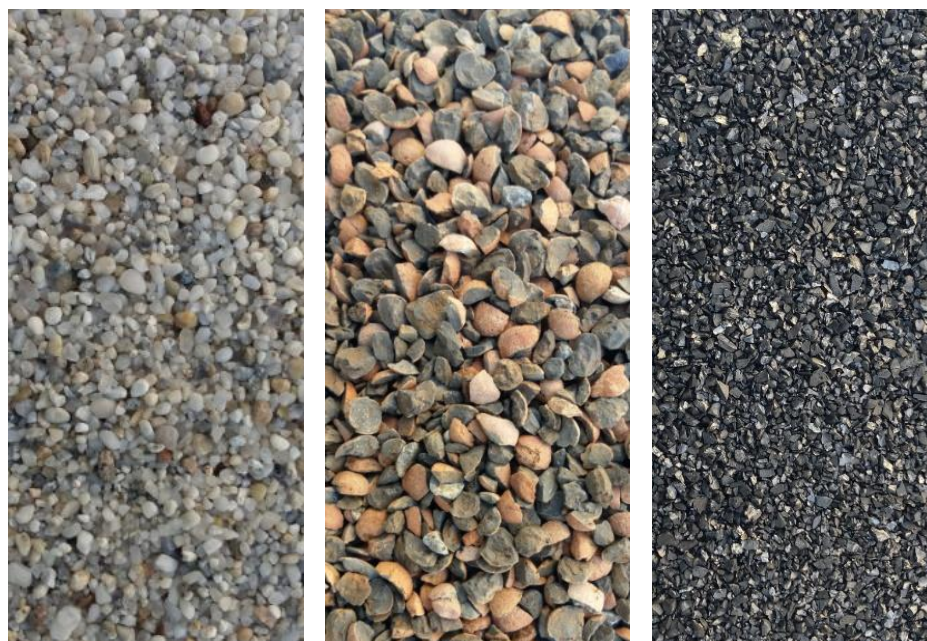
Figure 5.1. Technological scheme of biological filtration installation.

The filtration/support media used were: sand, ceramic granules and granular activated carbon. Their characteristics are presented in the following table:

Table 5.1. Filtration media characteristics.

Nr.	Filtration media	Granule dimensions [mm]	Filtration media height [m]	Filtration media volume [m ³]
1	Sand	0.95 ± 0.58	1.00	0.00785
2	Ceramic granules	3.28 ± 2.14	1.00	0.00785
3	Granular activated carbon	0.78 ± 0.60	1.00	0.00785

The support media used in the experimental research are presented in the following figure.



Sand

Ceramic granules

Granular activated carbon

Figure 5.2. Support/filtration media.

The filtering velocity corresponding to different flow rates introduced in the biological filters is presented in the following table.

Table 5.2. Filtering speed depending on operating flow.

Nr.	Flow		v_F (m/h)
	(l/h)	(m ³ /h)	
1	10	0.010	1.27
2	15	0.015	1.91
3	20	0.020	2.55
4	25	0.025	3.18
5	30	0.030	3.82
6	35	0.035	4.46
7	40	0.040	5.10

5.3 Analysis methods

To determine the raw water and biologically filtered water quality parameters, the existing equipment within the Colentina Laboratory Complex was used.

The following table presents the water quality parameters, analyzed in the experimental tests, but also the methods and equipment used in their determination.

Table 5.3. Raw water and filtered water analyzed quality parameters.

Nr.	Analyzed quality parameter	Reagents used	Method used	Lab equipment
1	Ammonium	Nessler reagent Mineral stabilizer Polyvinyl alcohol	HACH – USEPA ^a Nessler Method ^b	HACH spectrophotometer – DR3900
2	Nitrates	NitraVer 5 powder reagent	HACH - Cadmium Reduction Method	
3	Nitrites	NitriVer 3 powder reagent	HACH - USEPA Diazotization Method ^c	
4	Phosphorus	LCK 349 cuvette test	HACH - LCK349 Fosfor total / Fosfat orto	HACH spectrophotometer – DR3900 HACH dry heat thermostat with 2 blocks – LT200
5	pH	-	SR EN ISO 10523:2012	HACH digital laboratory multimeter with two-channel - HQ440D Marvel WTW PH-meter-pH526
6	Conductivity	-	SR EN 27888:1997	HACH digital laboratory multimeter with two-channel - HQ440D
7	Dissolved oxygen	-	SR EN 25813:2000/C91:2009	
8	Temperature	-	-	
9	Iron	FerroVer powder reagent	HACH – USEPA ^d FerroVer Method ^e	HACH spectrophotometer – DR3900
10	Alcalinity	Methyl orange Hydrochloric acid 0.1N	SR EN ISO 9963-1:2002	-
11	COD	Sulfuric acid 1:3 Potassium permanganate 0.01N Oxalic acid 0.01N	SR EN ISO 8467/2001	Electric heater

^a - USEPA accepted for wastewater analysis (distillation required), Method 350.2;

^b - adapted from Standard Methods for the Examination of Water and Wastewater, 4500-NH₃ B & C, 15th Edition;

^c - USEPA approved for wastewater analysis, Federal Register, 44(85), 25505 (May 1, 1979);

^d - USEPA approved for reporting wastewater analysis, Federal Register, June 27, 1980; 45 (126: 43459);

^e - adapted from Standard Methods for the Examination of Water and Wastewater.

The oxygen sensor and the chemical reagents used to determine the ammonium, nitrate, nitrite and phosphorus water quality parameters are part of a grant received from HACH LANGE S.R.L.

6. Experimental research results

6.1 Water used in experimental tests

Experimental research involved biological processes with biomass attached, and to help the biological process priming and maintain its stability, it was decided to use untreated water with potential for bacteriological development, which comes from a well near Bucharest.

The following table shows the raw water quality parameters from F1 well, used in the experimental tests.

Table 6.1. F1 raw water quality parameters.

Nr.	Water quality parameter	Minimum values	Average values	Maximum values
1	Ammonium [mg/l]	0.17	0.63	1.12
2	Nitrates [mg/l]	91.80	146.40	230.10
3	Nitrites [mg/l]	0.040	0.285	0.575
4	Phosphorus [mg/l]	0.029	0.032	0.036
5	Iron [mg/l]	0.020	0.025	0.030
6	Alkalinity [mval/l]	2.65	3.54	4.500
7	pH	6.71	7.78	8.24
8	Conductivity [μ S/cm]	845.00	1089.38	1327.00

According to results of the realised tests, the ammonium concentration in raw water from the F1 well varied during the tests between 0.17-1.12 mg/l.

Given that the existing ammonium concentration in raw water from well was maximum 1.12 mg/l and that in the tests it was proposed to determine the efficiency of the biofilters up to ammonium concentrations of 10 mg/l in influent, synthetic raw water was prepared. Raising the ammonium concentration in the raw water to the desired concentration was achieved by adding doses of ammonium chloride.

6.2 Biological process priming

Unlike other existing technologies for reducing the ammonium concentration in water, biofilters cannot be used immediately, and require a period of biological process priming. It was necessary a period of biological process priming, to carry out the experimental tests, respectively a period of bacteria growth necessary to reduce the ammonium in the water (*Nitrosomonas* și *Nitrobacter*).

During the biological process priming, the raw water used in the biological filtration process was replaced 3-4 times per week with fresh water from the F1 well.

6.3 Experimental stages

In the experimental tests, 3 test steps were proposed and performed, in which the biofilters efficiency in reducing the ammonium concentration in water was analyzed, depending on: the support media used for microorganisms attaching, the ammonium concentration in water and the contact time between water and attached biomass, as well as the analysis of the ammonium concentration variation in the filter layer of each biofilter.

The following table shows the raw water flows and the ammonium concentrations in the raw water from the 3 experimental stages.

Table 6.2. Experimental stages.

Stage	Test	Q _{raw} water [l/h]	Q _{raw} water/filter [l/h]	C _{ammonium} [mg/l]	Remarks
I	1	60	20	≈2	No phosphoric acid
	2	60	20	≈5	
	3	60	20	≈10	
II	1	105	35	≈2	
	2	105	35	≈5	
	3	105	35	≈10	
III	-	60	20	≈5	Test1 from stage I
	1	60	20	≈5	With the addition of phosphoric acid

The names used for ammonium concentrations in this doctoral thesis are

- low concentrations: 0.5-4 mg/l;
- average concentrations: 4-8 mg/l;
- high concentrations: 8-12 mg/l.

6.4 Working method during experimental research

After the biological process prime, the activity of performing the experimental tests started.

The biological process priming was verified by quality tests of raw water and biologically filtered water, checking in particular if the biofilters reduce the ammonium concentration in the water introduced in installation.

All experimental determinations were made in weekend, according to the following way of working:

- At the end of the week in which the biological process was started, raw water with the ammonium concentration in water and with the flow rate specific to test 1 from stage I was introduced in installation;
- After 2 hours, at the end of the first cycle of biological filtration, water samples were taken and the impact of sudden change of ammonium concentration in water was determined from the concentration in the priming period to that in test 1 stage I;
- Throughout the following week, the installation operated in a closed circuit, with the ammonium concentration and flow approximately equal to those in test 1, stage I;
- At the end of the next week, the experimental determinations corresponding to test 1 from stage I take place, regarding the determination of the biofilters efficiency in reducing the ammonium concentration in water and the variation of the ammonium concentration in the filter layer.
- On the same day, after the determinations of test 1 from stage I were closed, raw water with the ammonium concentration and flow rate specific to test 2 from stage I was introduced into the installation;
- After 2 hours (2 hours in stages I and III, respectively 1 hour in stage II) at the end of the first cycle of biological filtration water samples were taken and the impact of the sudden change of ammonium in water from test 1 stage I concentration to that of test 2 stage I;

- The steps listed above are followed for all tests.

The following figure shows laboratory images during the determination of water quality parameters for the taken samples.



Figure 6.1. Laboratory images, from water quality analysis

6.5 Experimental tests in stages I and II

6.5.1 Biofilters efficiency in reducing ammonium concentration in water

The determination of biofilters efficiency in reducing the ammonium concentration in raw water introduced in biofilters was achieved by determining the quality parameters for raw water and biological filtered water samples for each biofilter.

The biofilters operation was monitored by measurements of factors that influence the biological process, such as temperature, pH and dissolved oxygen.

6.5.1.1 Efficiency of reducing ammonium concentration in stage I

In the first stage, in each biofilter was introduced raw water with a flow rate of 20 l/h and 3 different concentrations of ammonium (one concentration for each test).

The following figure shows the ammonium retention efficiencies obtained on each biofilter depending on the ammonium concentration in water introduced into biofilters, after operation for one week with approximately equal ammonium concentration in raw water.

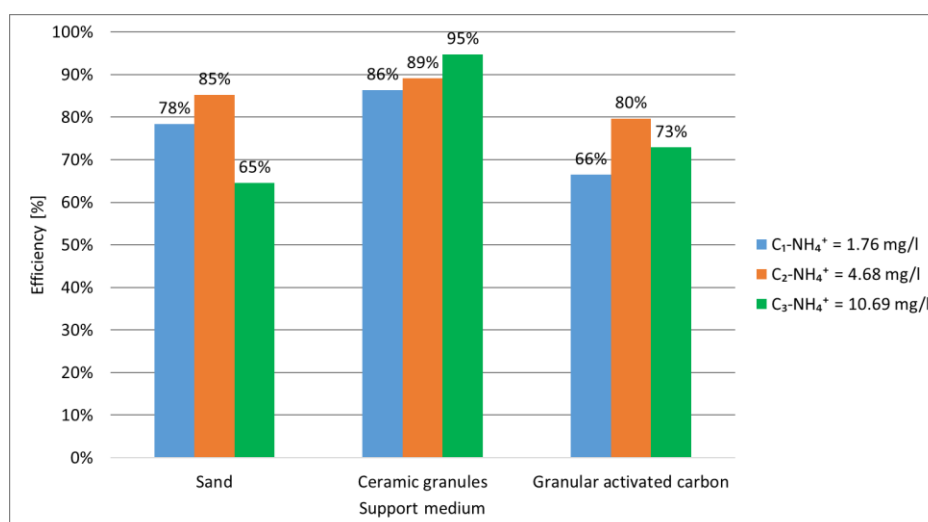


Figure 6.2. Efficiency of reducing the ammonium concentration in raw water in stage I.

According to the previous figure, at any ammonium concentrations in raw water introduced into the biofilters in step I, the highest efficiencies in reducing the ammonium concentration in water were obtained for the biofilter having ceramic granules as filtration media. For this biofilter, it is observed that if ammonium concentration in raw water is higher, the efficiency of the biofilter in reducing ammonium increases.

The biofilter used sand as support media has higher efficiencies in reducing ammonium at low (1.76 mg/l) and medium (4.68 mg/l) concentrations compared to the biofilter with granular activated carbon, and at high concentrations (10.69 mg/l), granular activated carbon biofilter is more efficient than sand biofilter.

For both, sand biofilter and granular activated carbon biofilter, the best efficiency is obtained at average ammonium concentrations in raw water.

The biofilters performance was not affected by temperature, pH and dissolved oxygen, the results obtained for these parameters being within the limits necessary for the biological process to function successfully.

6.5.1.2 Efficiency of reducing ammonium concentration in stage II

Stage II was similar to stage I, the only difference between the 2 stages being the reduction of the contact time between water and attached biomass, by increasing the water flow introduced in the installation. In this stage, raw water with a flow rate of 35 l/h and 3 different ammonium concentrations (one concentration for each test) was introduced into each biofilter.

The following figure shows the ammonium retention efficiencies obtained on each biofilter depending on the ammonium concentration in water introduced into biofilters, after operation for one week with approximately equal ammonium concentration in raw water.

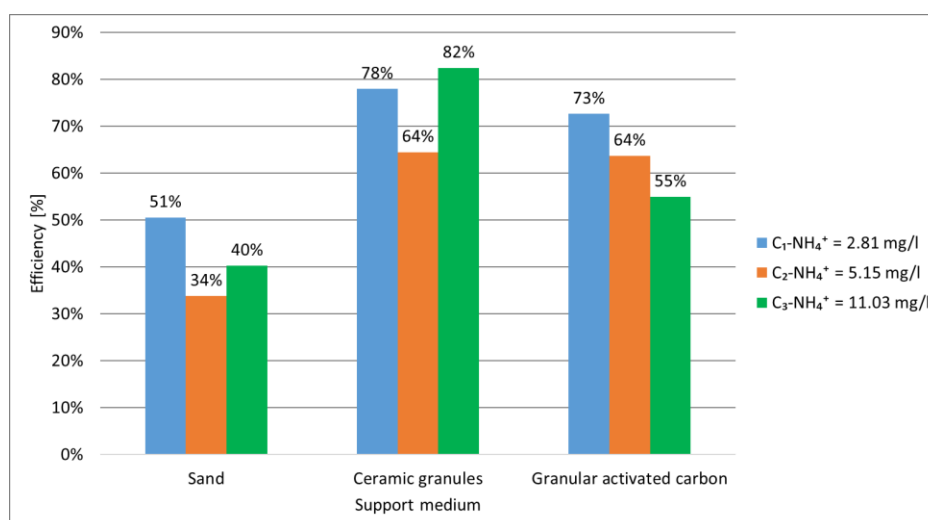


Figure 6.3. Efficiency of reducing the ammonium concentration in raw water in stage II.

According to the previous figure, it is observed that by reducing the contact time between water and attached biomass, the highest efficiencies in reducing ammonium were obtained for the biofilter with ceramic granules, followed by the biofilter with granular activated carbon and the biofilter with sand.

Comparing the results obtained in the 2 steps for the biofilter with ceramic granules, it is observed that in stage II, the efficiencies obtained in reducing ammonium are different from stage I. Thus, for low concentration ranges (2 mg/l the retention efficiency decreased from 86% to 78%), for medium concentration ranges (5 mg/l this decreased from 89% to 64%) and for high concentration range (10 mg/l this decreased from 95% to 82%). However, the highest efficiency result at high concentrations.

The biofilter that uses sand as a filtration media, the reduction of the contact time significantly influenced the retention efficiencies. Thus, for low concentration ranges (2 mg/l the retention efficiency decreased from 78% to 51%), for medium concentration ranges (5 mg/l it decreased from 85% to 34%) and for high concentrations (10 mg/l this decreased from 65% to 40%).

The biofilter with granular activated carbon is also affected by the reduced contact time. Thus, for low concentration domains (2 mg/l the retention efficiency increased from 66% to 73%), for medium concentration domains (5 mg/l it decreased from 80% to 64%) and for high concentrations (10 mg/l this decreased from 73% to 55%).

For the granular activated carbon biofilter, it is observed that as the ammonia concentration in the raw water increases, the efficiency of the biofilter in reducing the ammonium concentration decreases.

Comparing the efficiencies obtained in stage I with those obtained in stage II, a decrease is observed in stage II, due to the reduction of the contact time between water and the attached biomass, but at the same time it can be observed that in case of reduction of contact time, the best efficiencies in reducing ammonia are represented by the biofilter that has ceramic granules, as a support medium.

Similar to stage I, in stage II pH, temperature, dissolved oxygen and conductivity were within the limits necessary for the functioning of the biological nitrification process. The concentration of phosphorus in the raw water was reduced insignificantly after biological filtration.

6.5.2 The impact of sudden change in the ammonium concentration in raw water on the biofilters efficiency in reducing ammonium concentration in water

These tests looked at the impact of a sudden change of the ammonium concentration in synthetic water on the efficiency of biofilters. That is, how biofilters behave when switching from one concentration to another.

The following figure shows the efficiencies obtained on each biofilter in order to reduce the ammonium concentration in water, depending on the biofilters support media and on the ammonium concentration in water introduced into the biofilters, when the ammonium concentration suddenly changes.

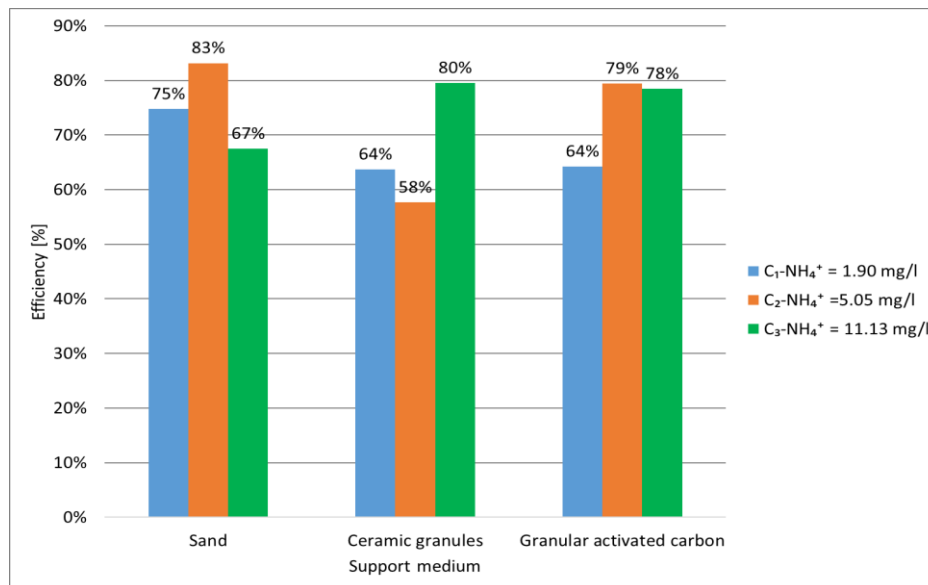


Figure 6.4. Efficiency of reducing the ammonium concentration depending on the filtration media used and the ammonium concentration in the raw water introduced in biofilters, at sudden change of ammonium concentration - phase I.

The following figure shows the efficiencies obtained on each biofilter in order to reduce the ammonium concentration in water, depending on the biofilters support media and on the ammonium concentration in water introduced into the biofilters, when the ammonium concentration suddenly changes.

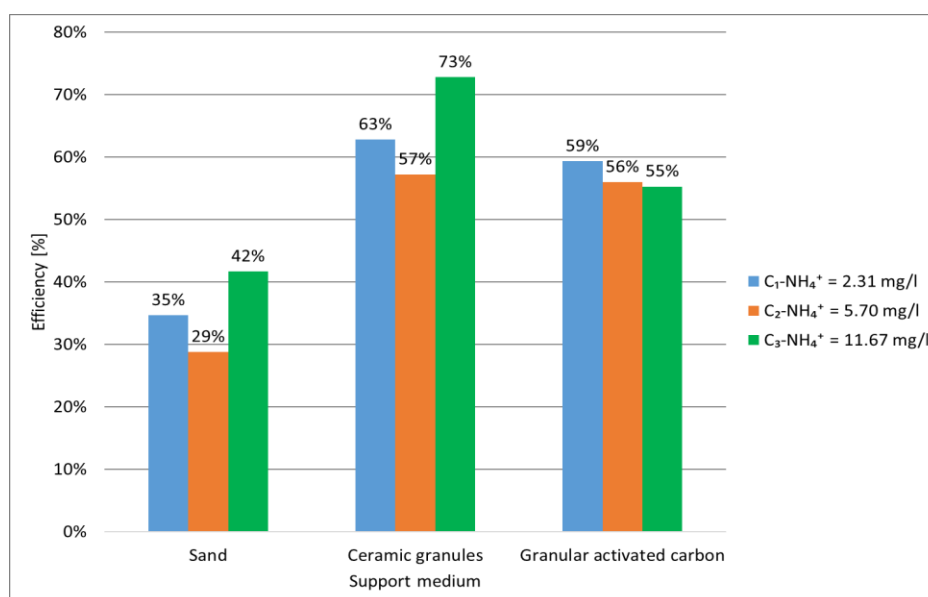


Figure 6.5. Efficiency of reducing the ammonium concentration depending on the filtration media used and the ammonium concentration in the raw water introduced in biofilters, at sudden change of ammonium concentration - phase II.

Given that there are no massive decreases in the biofilters efficiency, when the concentration of ammonium in the raw water changes suddenly, these results from the sudden change in the concentration of ammonium in the water do not accurately reflect the efficiency of the biofilters, it is possible that after a few hours of operation the biofilter with ceramic granules to obtain efficiencies similar to the previous ones.

6.5.3 Variation of ammonium concentration in filter layer

At the same time as determining the efficiency of the biofilters in reducing the concentration of ammonium in the raw water introduced in installation, the variation of the ammonium concentration in the filter layer was also determined. This variation was determined only for the sand biofilter and the ceramic grain biofilter.

6.5.3.1 Variation of ammonium concentration in filter layer in the biofilter with sand

6.5.3.1.1 Variation of ammonium concentration in filter layer depending on the ammonium concentration in raw water

To determine the variation of ammonium concentration in filter layer, water samples were taken from 4 points, filter inlet, lower layer ($H = 0.3 \text{ m}$), upper layer ($H = 0.7 \text{ m}$) and from filter outlet ($H = 1 \text{ m}$). The water samples from biofilter inlet and outlet are water samples for which the efficiency of reducing the ammonium concentration in water has also been determined.

The following figures show the variation of the ammonium concentration in the filter layer, when raw water with three different ammonium concentrations and a constant flow of 20 l/h is introduced into the biofilter.

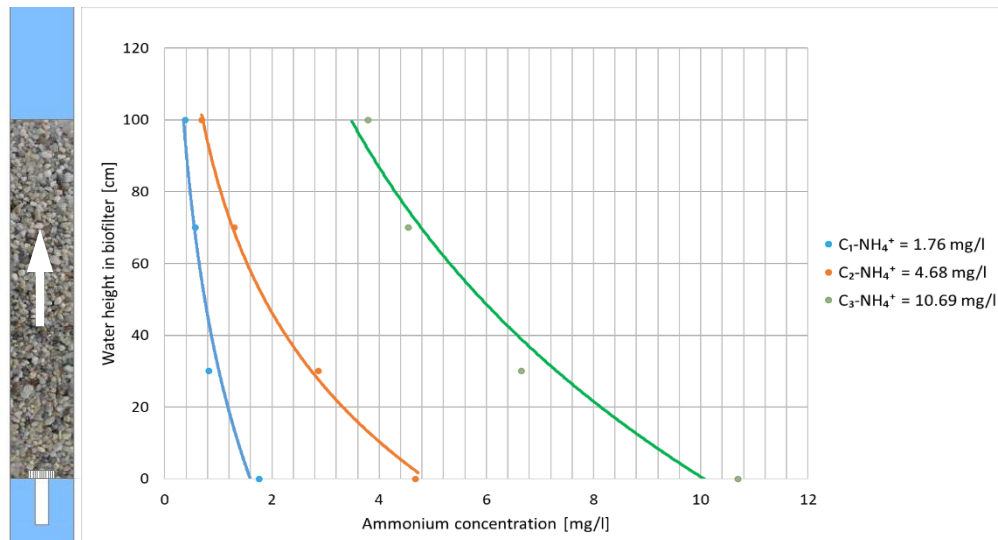


Figure 6.6. Variation of ammonium concentration in the filter layer for the biofilter with sand in stage I.

As can be seen in the figure above, at any ammonium concentration in raw water, ammonium is oxidized mostly in the lower layer, followed by the middle layer and the upper layer, resulting that the most active bacteria being in the lower layer. It can be observed that in the case of concentrations of 1.76 mg/l and 4.68 mg/l of ammonium in prepared raw water, the ammonium concentration in biologically filtered water is reduced to below or near the maximum permissible limit according to Law 458/2002, and in the case of a concentration of 10.69 mg/l, the ammonium concentration after biological filtration is reduced to 3.79 mg/l.

The following figure shows the variation of the ammonium concentration in the filter layer, when raw water with three different ammonium concentrations and a constant flow of 35 l/h is introduced into the biofilter.

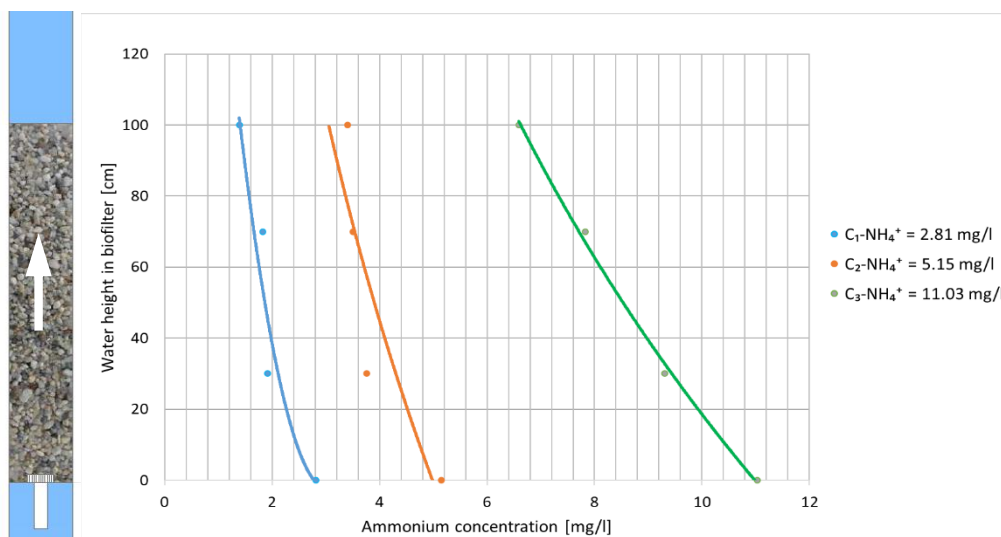


Figure 6.7. Variation of ammonium concentration in the filter layer for the biofilter with sand in stage II.

As can be seen in the previous figure, the ammonium concentration is best reduced in the lower layer. Another aspect that demonstrates that the attached biomass in the lower layer is the most active, is represented by the variation of the efficiency in reducing the ammonium concentration in the filter layer.

6.5.3.1.2 Variation of ammonium concentration in filter layer depending on the raw water flow introduced in the installation

The following figures show the variation of ammonium concentration in the filter layer in the 2 steps. The purpose of these figures is to observe exactly the impact of reducing the contact time between water and the attached biomass, separately for each concentration range.

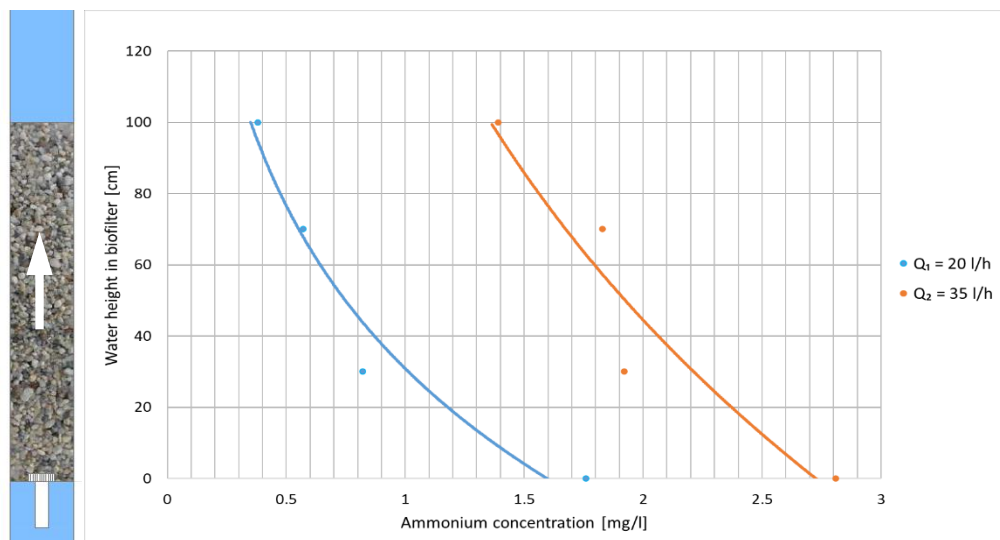


Figure 6.8. Variation of ammonium concentration in the filter layer in stages I and II for the biofilter with sand – low ammonium concentrations (1.76 si 2.81 mg/l) in raw water.

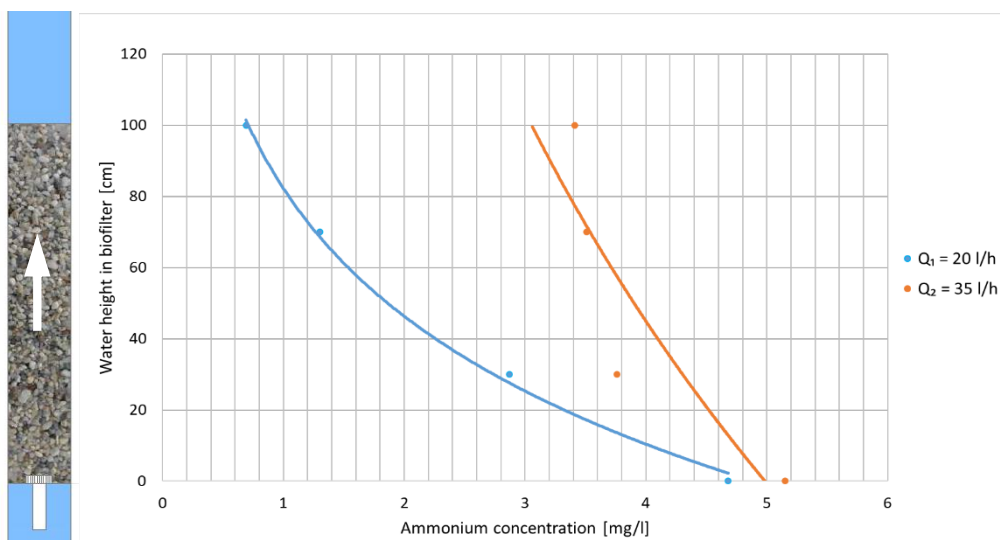


Figure 6.9. Variation of ammonium concentration in the filter layer in stages I and II for the biofilter with sand – average ammonium concentrations (4.68 si 5.15 mg/l) in raw water.

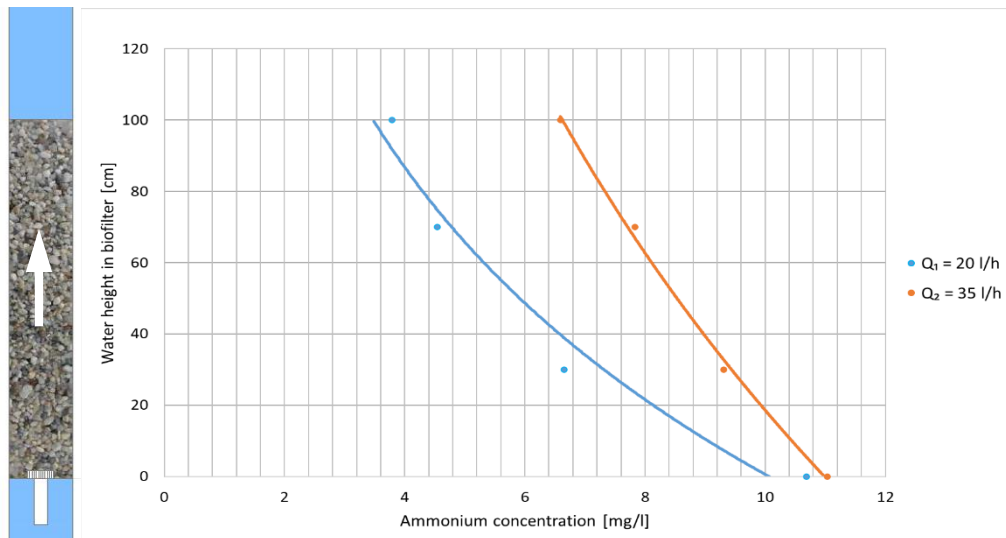


Figure 6.10. Variation of ammonium concentration in the filter layer in stages I and II for the biofilter with sand – high ammonium concentrations (10.69 si 11.03 mg/l) in raw water.

As can be seen in the previous figures, an increase in the raw water flow decreases the contact time between water and attached biomass, leading to a decrease in the biofilters efficiency in reducing the ammonium concentrations in water. It can also be seen that the lower layer is less affected by the reduced contact time between water and attached biomass.

6.5.3.2 Variation of ammonium concentration in filter layer in the biofilter with ceramic granules

6.5.3.2.1 Variation of ammonium concentration in filter layer depending on the ammonium concentration in raw water

To determine the variation of ammonium concentration in filter layer, water samples were taken from 4 points, filter inlet, lower layer ($H = 0.3 \text{ m}$), upper layer ($H = 0.7 \text{ m}$) and from filter outlet ($H = 1 \text{ m}$). The water samples from biofilter inlet and outlet are water samples for which the efficiency of reducing the ammonium concentration in water has also been determined.

The following figures show the variation of the ammonium concentration in the filter layer, when raw water with three different ammonium concentrations and a constant flow of 20 l/h is introduced into the biofilter.

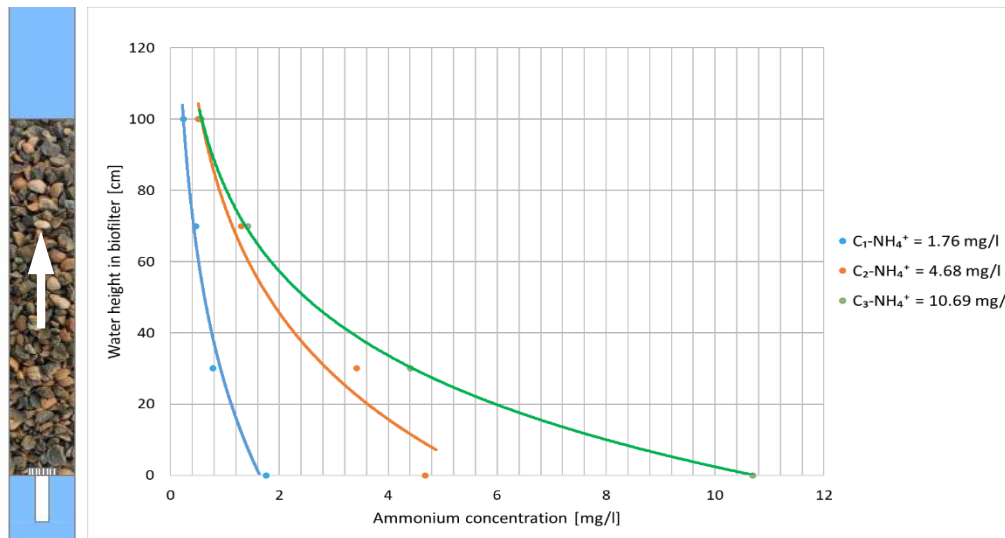


Figure 6.11. Variation of ammonium concentration in the filter layer for the biofilter with ceramic granules in stage I.

As can be seen in the figure above, for all 3 ammonium concentrations in raw water introduced into the biofilter, the ammonium concentration is more reduced in the lower layer, followed by the middle layer and the upper layer, resulting that the most active bacteria are located in the lower layer.

The following figure shows the variation of the ammonium concentration in the filter layer, when raw water with three different ammonium concentrations and a constant flow of 35 l/h is introduced into the biofilter.

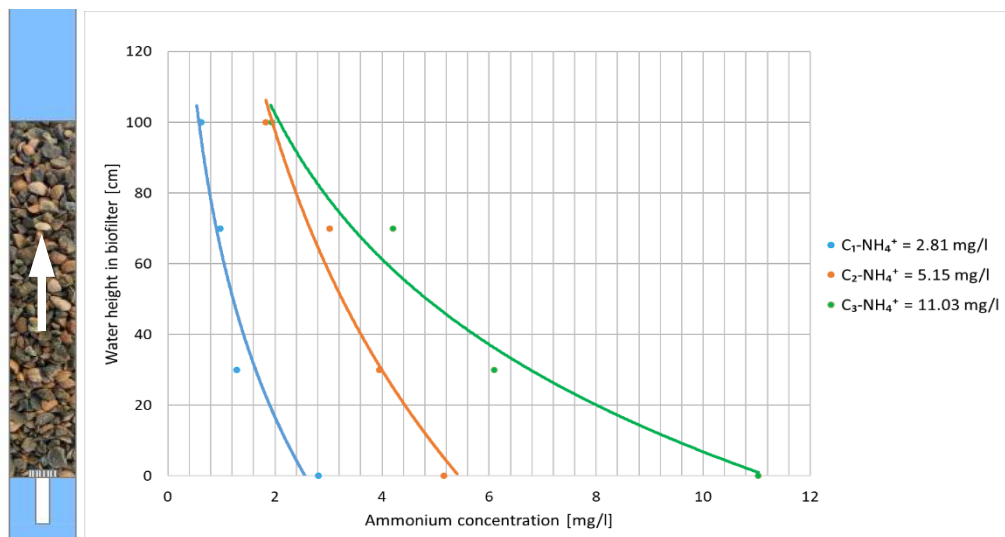


Figure 6.12. Variation of ammonium concentration in the filter layer for the biofilter with ceramic granules in stage II.

According to the previous figure, at any ammonium concentration in raw water introduced into biofilter, the ammonium concentration is reduced mostly in the lower layer, followed by the upper layer and the middle layer, resulting that the most active bacteria are in the lower layer. It can be seen that depending on the ammonium concentration in raw water, it is reduced in larger quantities to higher concentrations. It can be observed that in the case of an ammonium concentration of 2.81 mg/l in raw water, after biological filtration the ammonium concentration is

reduced close to the maximum permissible limit according to Law 458/2002 (at a difference of less than 0.15 mg/l), and in the case of concentrations of 5.15 and 11.03 mg/l in raw water, the ammonium concentration in biologically filtered water is reduced below 2 mg/l.

6.5.3.2.2 Variation of ammonium concentration in filter layer depending on the raw water flow introduced in the installation

The following figures show the variation of the ammonium concentration in the filter layer, depending on the raw water flow introduced in the biofilter.

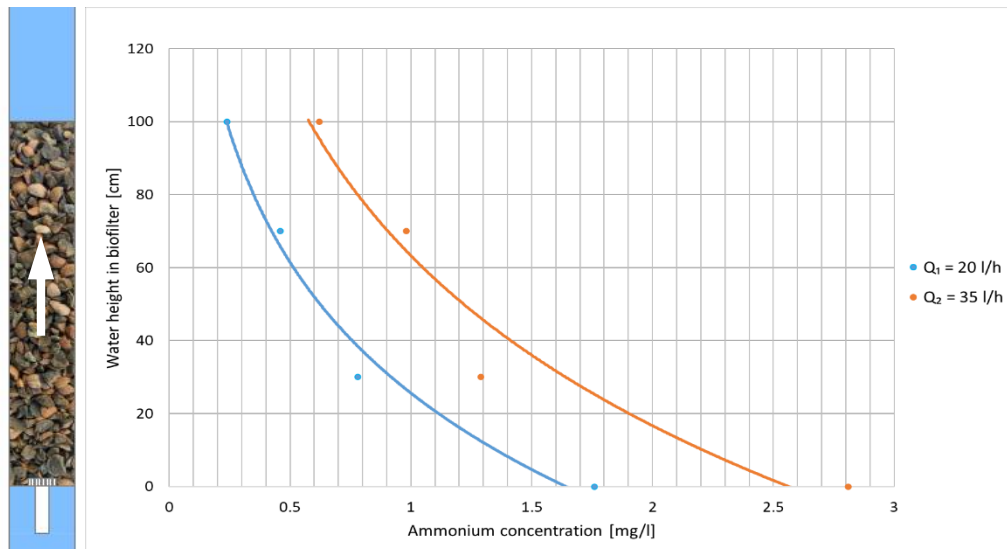


Figure 6.13. Variation of ammonium concentration in the filter layer in stages I and II for the biofilter with ceramic granules – low ammonium concentrations (1.76 si 2.81 mg/l) in raw water.

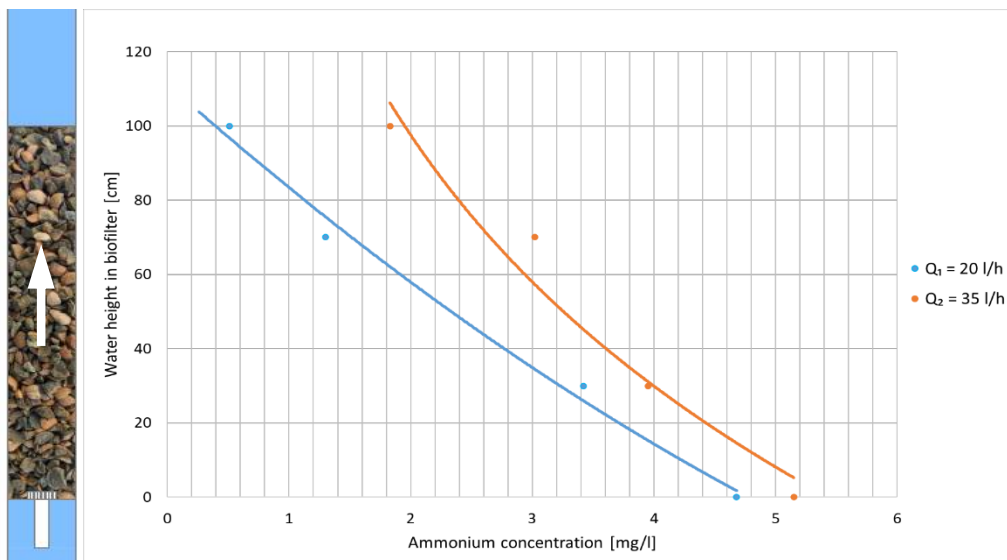


Figure 6.14. Variation of ammonium concentration in the filter layer in stages I and II for the biofilter with ceramic granules – average ammonium concentrations (4.68 si 5.15 mg/l) in raw water.

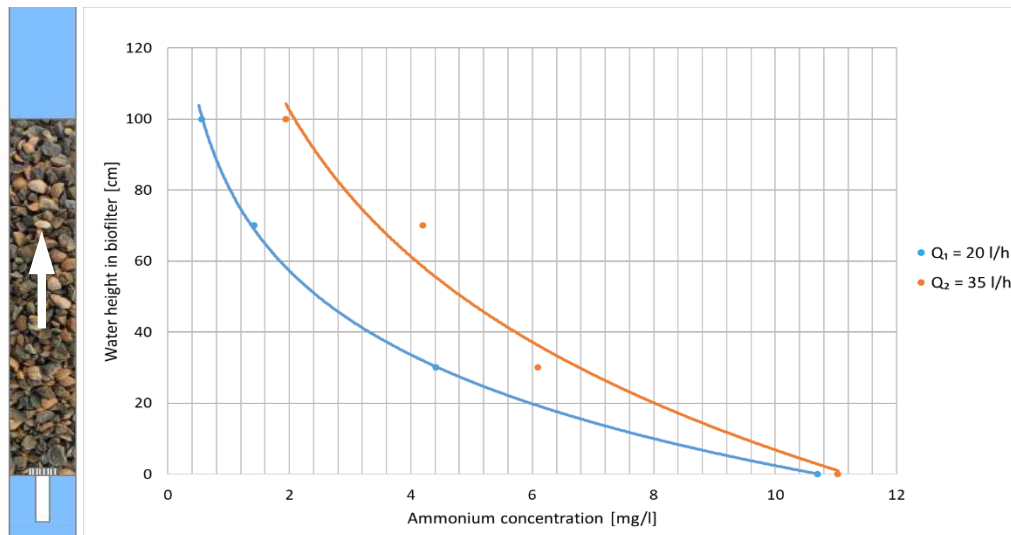


Figure 6.15. Variation of ammonium concentration in the filter layer in stages I and II for the biofilter with ceramic granules – high ammonium concentrations (10.69 si 11.03 mg/l) in raw water.

As can be seen in the previous figures, an increase in the raw water flow decreases the contact time between water and attached biomass, leading to a decrease in the biofilters efficiency in reducing the ammonium concentrations in water. It can also be seen that the lower layer is less affected by the reduced contact time between water and attached biomass.

Comparing the results of stage II obtained for the biofilter with sand and for the biofilter with ceramic granules, it can be said that the biofilter with ceramic granules is less affected by the reduction of the contact time between water and attached biomass..

6.6 Experimental test results in stage III

In the tests performed in stages I and II it was observed that for any ammonium concentration in raw water, after biological filtration, the ammonium concentration does not fall below the minimum value obtained of 0.24 mg/l.

In the first phases it was also observed that the concentration of phosphorus in water is very low, phosphorus being a necessary nutrient in the nitrification process. For this reason, in this phase, a new test was performed, with the addition of phosphoric acid (0.26 mg/l) in the synthetic raw water, to check if a better efficiency in reducing ammonium is obtained.

In order to be able to compare the results obtained with the previous tests, the same water flow (20 l/h on each filter) was used and a concentration approximately equal to 5 mg/l, respectively the raw water flow and the ammonium concentration in the water, were approximately equal to those in test 2, from phase I.

The following figure shows the efficiencies obtained for biological filtration in phase III.

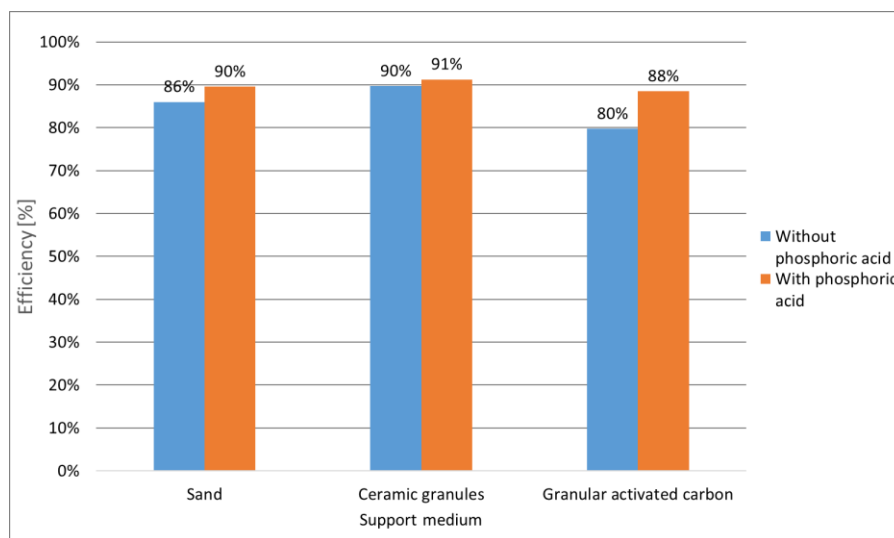


Figure 6.16. Efficiency of reducing the ammonium concentration in raw water in stage III.

Comparing the results obtained regarding the efficiencies of the biological process in reducing ammonium for normal operation and operation with the addition of phosphoric acid, it is observed that similar efficiencies are obtained in both cases, with one small exception, a small increase in ammonium concentration reduction efficiency for raw water with phosphoric acid.

It was tried the increase of the efficiency by doubling the dose of phosphoric acid, but still no significantly higher efficiencies were obtained.

The following figures show the variation of the ammonium concentration in the filter layer in stage III, when raw water with an ammonium concentration of approximately 5 mg/l and a constant flow rate of 20 l/h is introduced into the biofilter.

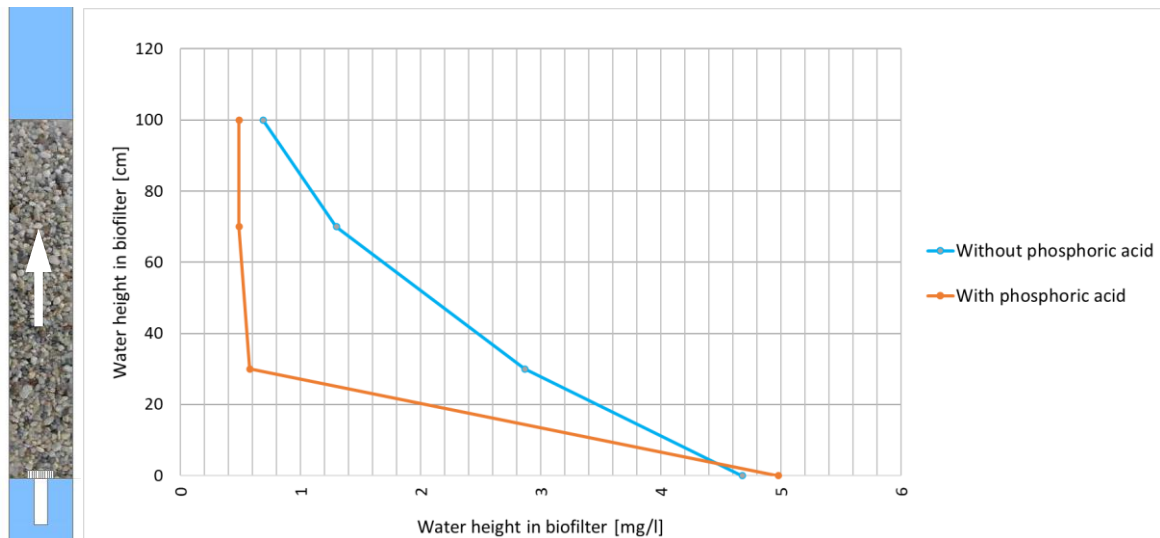


Figure 6.17. Variation of ammonium concentration in biofilter with sand in stage III.

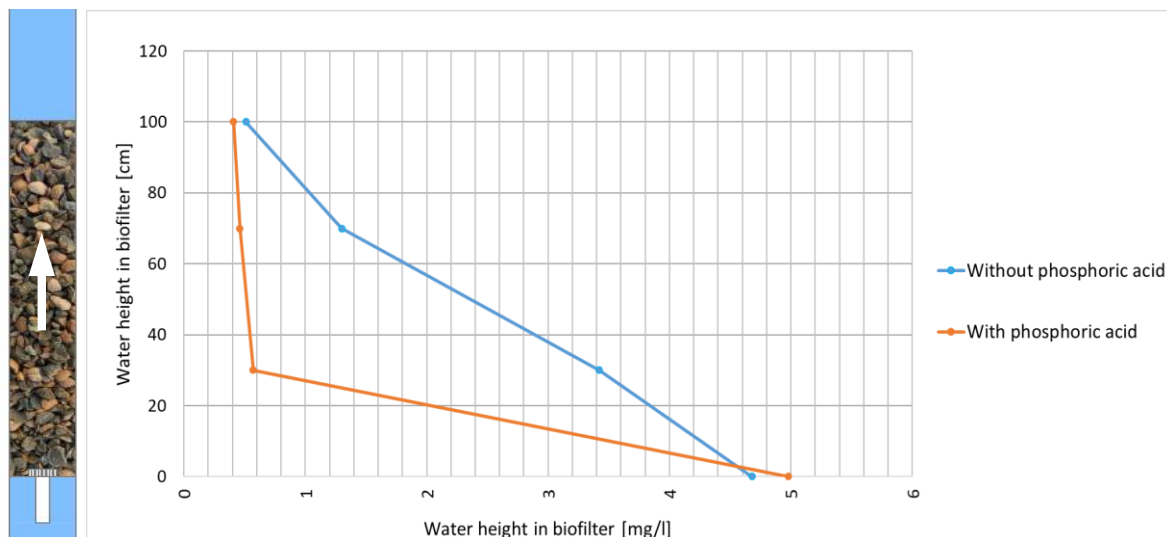


Figure 6.18. Variation of ammonium concentration in biofilter with ceramic granules in stage III.

In the previous figures, it can be seen that in both media used, the concentration of ammonium in biofilters varies approximately constantly for raw water without the addition of phosphoric acid, but in the case of raw water with the addition of phosphoric acid, phosphorus is consumed in the first centimeters of the filter layer (first contact area), an area where the ammonium concentration drops sharply and then remains approximately constant until the biofilter outlet. In the case of fractional introduction of phosphoric acid at the height of the filter layer, it is possible that the attached biomass will be better stimulated, which would lead to an even better biofilter efficiency in the retention of ammonium.

7. General conclusions

The support media used were: sand, ceramic granules and granular activated carbon..

Synthetic raw water prepared from groundwater with a maximum ammonium concentration of 1.12 mg/l was used in which ammonium chloride was added to obtain the desired concentrations for experimental research: 2 mg/l, 5 mg/l and 10 mg/l.

During the experimental tests, 3 stages were performed, in which the biofilters efficiency in reducing the ammonium concentration in water was analyzed, depending on: the support medium used for the microorganisms attachment, the ammonium concentration in water and the contact time between water and attached biomass, as well as the analysis ammonium concentration variation in the filter layer of each biofilter.

According to the results obtained from experimental research, the following can be stated:

- The biological nitrification process worked throughout the experimental tests, considering that a reduction of the ammonium concentration was found at the same time as an increase of the nitrate concentration in the treated water, which indicates the ammonium oxidation to nitrate;
- The results obtained after the installation operation for a week with an approximately constant ammonium concentration in raw water, indicate that in all tests in the three stages, biofilters using ceramic granules as support media have the highest efficiency in reducing ammonium concentrations in water (between 64% and 95%);
- All biofilters are affected by the reduction of the contact time between water and attached biomass, because according to the obtained results, simultaneously with the contact time decrease there was a decrease of the biofilters efficiency in reducing the ammonium concentration in raw water. In all tests in stages I and II, the biofilter with ceramic granules was the least affected by the contact time reduction between the water and attached biomass.
- From the point of view of the ammonium concentration variation in the filter layer, it can be stated that in all tests in the three stages, the ammonium concentration is best reduced in the lower layer, resulting that the most active and efficient biofilter area is the first contact zone;
- The biological process total efficiency is not significantly improved by the addition of nutrients, but in the case of their addition (phosphoric acid), there is a significant increase in the activity of the biofilters lower layer;
- The efficiencies of reducing the ammonium concentrations on biological filter with ceramic granules as filter layer, can be classified as follows:
 - At filtering speed $v_F = 2.55 \text{ m/h}$:
 - NH_4^+ concentration in raw water: $C_{AB} = 1.76 \text{ mg/l}$;
 - NH_4^+ concentration in filtered water: $C_{AF} = 0.24 \text{ mg/l}$;
 - NH_4^+ concentration in raw water: $C_{AB} = 4.68 \text{ mg/l}$;
 - NH_4^+ concentration in filtered water: $C_{AF} = 0.51 \text{ mg/l}$;
 - NH_4^+ concentration in raw water: $C_{AB} = 10.69 \text{ mg/l}$;
 - NH_4^+ concentration in filtered water: $C_{AF} = 0.56 \text{ mg/l}$;
 - At filtering speed $v_F = 4.46 \text{ m/h}$:
 - NH_4^+ concentration in raw water: $C_{AB} = 2.81 \text{ mg/l}$;
 - NH_4^+ concentration in filtered water: $C_{AF} = 0.62 \text{ mg/l}$;
 - NH_4^+ concentration in raw water: $C_{AB} = 5.15 \text{ mg/l}$;
 - NH_4^+ concentration in filtered water: $C_{AF} = 1.83 \text{ mg/l}$;

- NH_4^+ concentration in raw water: $C_{AB} = 11.03 \text{ mg/l}$;
 - NH_4^+ concentration in filtered water: $C_{AF} = 1.94 \text{ mg/l}$.
- Based on the results of experimental research, it can be said that biofilters can be used successfully in reducing ammonium concentrations in water, require low operating costs, and in the case of effluent concentrations that exceed but are still close to the limit, a secondary treatment can be done with breakpoint chlorination, in which case the required doses of chlorine are much lower than the doses required for direct ammonium oxidation in raw water (without biofilters), resulting in an extremely low risk of the formation of trihalomethane (THM) reaction by-products toxic to the human body.

7.1 Personal contributions and elements of originality

The elements of originality and personal contributions obtained in this doctoral thesis are:

- Comparative analysis of the three filter media efficiency in reducing ammonia through biological filtration processes: sand, ceramic granules and activated carbon;
- All the analyzed media can be used to reduce the ammonium concentrations in water, but in the case of using ceramic granules as the biofilter support media, the highest efficiencies were obtained;
- Testing the biological process resistance to the sudden increase of the raw water load, either by increasing the ammonium concentration in the raw water, or by increasing the raw water flow; the results of these biological resistance tests indicate the following:
 - Biofilters are affected by the sudden change of ammonium concentration in introduced raw water, but overall, the efficiency of ammonium oxidation is preserved;
 - The biofilters efficiency registers significant decreases at the contact time reduction between water and attached biomass, respectively at the filtration speed increase;
 - The maximum permissible concentration ranges for which biological filters with ceramic granules operate efficiently and can reach concentrations that fall within the limits provided by the Drinking Water Law (0.5 mg/l), according to the research are:
 - At filtration speed $v_F < 2.50 \text{ m/h}$, the ammonium concentration in raw water can be $C_{AB} \leq 10.0 \text{ mg/l}$;
 - At filtration speed $v_F < 4.50 \text{ m/h}$, the ammonium concentration in raw water can be $C_{AB} \leq 2.50 \text{ mg/l}$;

Experiments have shown that biological activity is not evenly distributed over the height of the filter layer. The first contact area between water and attached biomass (the first 20 cm of the biological reactor) is the most active and implicitly the most efficient area in the biofilters, the ammonium concentration in water being reduced in a very high proportion (up to 80% of the total reduction on the entire biofilter) in this area

The results of the doctoral thesis were capitalized by the publication of several articles, among which are mentioned:

- Radu, Ghe. & Racoviteanu, G. - *Removing ammonium from water intended for human consumption. A review of existing technologies*, 7th Conference of the Conference of the Sustainable Solutions for Energy and Environment (EENVIRO 2020) - IOP Conference Series: Earth and Environmental Science, Volume 664, Issue 1, 2021;

- Radu, Ghe., Racoviteanu, G., Vulpasu, E. & Vlad, C. - *Kinetics and chemistry of nitrification process – A review*, Modeling in Civil and Environmental Engineering, Volume 16, Issue 3, 2021;
- Radu, Ghe., Racoviteanu, G. & Vulpasu, E. - *Biofilters efficiency in removing ammonium from water intended for human consumption*, Revista Romana de Inginerie Civila, Volume 13, Issue 2, 2022.

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