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RESEARCH REPORT NO. 3
Experimental research on water treatment technologies to reduce nitrogen concentrations

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Abbreviation

NH_4^+	Ammonia ion
NO_3	Nitrate
N_2	Nitrogen
O_2	Oxygen
SLD	Under detection limit
EPA	Environmental Protection Agency

1 Nitrate. Generalities

1.1 Nitrogen in water

Depending on the nature and oxidation state in which they are found, nitrogen compounds exist in many forms in natural waters (surface or groundwater). They can be dissolved (mineral or organic), colloidal or free [1].

Depending on the oxidation state, nitrogen compounds exist in one or more forms such as ammonia, ammonium ion, molecular nitrogen, nitrite ion, nitrate ion, and salts [1].

Nitrate is a chemical compound made up of a nitrogen atom attached to three oxygen atoms, designated by the symbol "NO_3^-". It is the main source of nitrogen for plants, being a nutrient without which they cannot grow. Intensive agriculture can deplete soil resources, so farmers add nitrogen-based fertilizers. In the case of careful management of the amounts of nitrogen used in agriculture, the quality of natural waters is not endangered and crops have high yields. However, if the amount of nitrate added is greater than the plant needs, the excess nitrate seeps into groundwater and contaminates it.

Usually, the concentration of nitrates in surface waters is low, ranging from 0-18 mg/l, but can reach much higher values in the case of farms, industrial discharges, or discharges of insufficiently treated wastewater [2].

1.2 Sources of pollution with nitrogen compounds

High concentrations of nitrates in surface sources originate in a multitude of sources, many of which depend on human activities and therefore vary by region and time.

The main sources of pollution of surface water sources with nitrates are represented by:

- Agricultural activities;
- Insufficiently treated wastewater, discharged into surface water.

In practice, seasonal changes in nitrate concentrations in surface waters have been observed. Nitrogen concentration is lower in summer and autumn and higher in winter and spring. Concentration increases during melting snow and during heavy storms, when the soil is "washed" by water from melting snow or rain.

The presence of ammonium in the water and the lack of nitrite indicate recent pollution of the water. When water contains both ammonium and nitrogen, pollution is assumed to have elapsed over a while. The lack of the presence of nitrates and nitrites implies long-standing impurity.

In surface waters, a consequence of pollution with nitrogen-based compounds is eutrophication, which is defined as the excessive development of algae and higher plant species, caused by the enrichment of water with nutrients.

Groundwater sources usually contain higher concentrations of nitrogen compounds than surface water sources.

Nitrogen concentrations in underground sources have increased over the years for several reasons. The main reasons that led to these increases are represented by the intensive agriculture and the building of centralized water supply systems, without building the sewerage systems for the localities. In many areas of the country, the concentrations of nitrates in raw water have values well above the limit imposed by law 458/2002 on drinking water quality, 50 mg / l. [3]

Intensive agriculture is considered to be the main source of nitrogen pollution in groundwater. As the demand for food increases and the principle of crop rotation is no longer sustainable, the soil is depleted of resources; because of this, fertilizers are used to replenish the nutrient reserves of plants in the soil. In many European countries, studies have shown that in areas

where intensive agriculture is practiced, most groundwater contains high concentrations of nitrates. Regarding the fertilizers used in agriculture, it is estimated that only 40 - 60% of the total amount is used by plants, the rest reaching the water sources. [4]

1.3 The effects of nitrogen compounds on the human health

In water supply systems, the presence of excess nitrogen compounds in raw water is undesirable because it can cause problems such as unpleasant odors, promotes microbial development in the water distribution system, reduces the efficiency of chlorine disinfection, and increases chlorine consumption.

Nitrogen or nitrate converted to nitrite in the body causes two chemical reactions that can cause adverse health effects: induction of methemoglobinemia, especially in infants under one year of age, and the potentially carcinogenic formation of nitrosamides and nitrosamines [5].

Nitrogen is a less dangerous form for adults, but for newborns, it can cause methemoglobinemia - "blue baby syndrome" [5]. Nitrates as such are not toxic, for them to become dangerous to the newborn's body they must be converted to nitrite. Once in the blood, nitrites combine with hemoglobin, forming methemoglobin, and blocking the transport of oxygen to tissues.

The lethal dose of nitrates for humans varies between 67 and 833 mg/kg and 33 to 250 mg/kg or nitrites [5].

Methemoglobin, normally present in 1 to 3 percent of the blood, is oxidized and cannot act as a carrier of oxygen in the blood. Certain substances, such as nitrite, are formed by the reaction of nitrate with saliva, but in infants less than one-year-old, less acidic conditions in the stomach allow bacteria to form nitrite. Up to 100% of nitrate is reduced to nitrite in infants, compared to 10% in adults and children over one year of age.

In addition, newborns do not have the same ability as adults to convert methemoglobin back to hemoglobin. When the concentration of methemoglobin reaches 5-10%, the symptoms may include lethargy, suffocation, and blue skin coloration - "blue baby syndrome". Anoxia and death can occur at high concentrations of nitrates or nitrites. However, this is quite rare. According to the WHO, since 1945, there have been about 2,000 cases of illness, about 8% of which have resulted in death [5].

Nitrosamines and nitrosamides are formed when nitrates react with nitrosable amines, such as amino acids in proteins. However, epidemiological studies, mainly on gastric cancer, have not yielded consistent results. Nitrogen carcinogenicity studies are currently being reviewed.

It is estimated that about 30% of all nitrogen compounds ingested by humans come from water.

In the case of intensive agriculture, high doses of fertilizers can lead to the storage of nitrogen by plants. Thus, vegetables such as spinach and carrots are likely to accumulate nitrogen in their component [6].

Some studies suggest that in large amounts in drinking water, nitrates can have effects such as miscarriages and problems for newborns whose mothers have been exposed to high concentrations of nitrates during pregnancy. Three epidemiological studies (Kostraba et al. 2000, Parslow et al. 1997, van Maanen et al. 2000) suggest a link between high concentrations of nitrates in drinking water and type 1 diabetes in children [7].

In 2016, a study was conducted on postmenopausal women diagnosed with bladder cancer between 1986 and 2010. The study found that there is a direct link between bladder cancer and water consumption. drinking water that contains high concentrations of nitrates [7].

Current studies suggest that exposure to high concentrations of nitrates (greater than 50 mg/l) for a long time may lead to thyroid problems, but epidemiological studies on the link between nitrate intake and thyroid problems don't have consistent results. Studies on the effect on the thyroid gland are under review [5].

Nitrogen-containing pollutants also have negative effects on the aquatic environment, leading to the eutrophication of lakes and the accelerated and massive development of microplankton and aquatic vegetation.

In Romania, the maximum permissible limit for nitrogen in drinking water, according to law 458/2002, is 50 mg / l. The guideline level according to the World Health Organization (WHO 2011) for ammonium is 50 mg / l [1] [3].

According to the EPA, the maximum allowable limit for nitrates in drinking water is 10 mg N/l. [8]

2 Technologies used to reduce nitrates in water

Over time, several methods have been developed to reduce the concentration of nitrates in water intended for human consumption.

If the raw water contains nitrogen concentrations above the limit imposed by law, two alternatives can be considered: water treatment or non-treatment.

Some techniques do not involve water treatment, the main methods used are mixing water with good quality water or abandoning the source. By mixing water with a high content of nitrates with water with a low content of nitrates dissolved in water, a ter with a concentration of nitrogen is obtained located below the limit imposed by the legislation in force [6].

If there is an alternative source of water that can provide the required amount of water and the quality of water from this source is superior to that from the source polluted with nitrogen, you can choose to use the alternative source of water and abandon the source that contains nitrogen. In this case, it is possible to opt for the temporary inactivation of the existing source, to be able to reactivate the source, and to be able to resume the water supply from the initial source at any time. This is recommended when nitrogen pollution is short-lived or if the water supply system will be equipped with a treatment plant that can remove nitrogen from drinking water, but for various reasons, this will not happen immediately. [6].

If the source of water containing high concentrations of nitrogen is not used in the future, the source may be abandoned and inactivated to eliminate the risk of distributing water that may be a danger to those who use it. In these cases, the water from that source can be used for other purposes, for example, in agriculture. The high concentration of nitrates is an advantage in this case. In the case of decommissioning an underground source, the costs vary depending on the number of wells, the depth of the wells, their diameter, and location [6].

In most cases, the use of an alternative source of water is not possible, and it is mandatory to treat the water before it is distributed to consumers. The main treatment processes applicable to sources that exceed nitrates are:

Biological processes - are based on the development of specific biomass for denitrification; To maintain the biomass, a food source must be added for the bacteria, usually, methanol being used, which means an increase in the concentration of total organic carbon and implicitly the risk of the formation of THM, which are carcinogenic. The process is unstable, it must be controlled very rigorously, it is very sensitive to inhibitory substances, the initiation of the process with biomass recovery takes about a month and if the biomass is lost, the process must be stopped during its regeneration [5].

Ion exchangers - there are masses of ion exchangers specially dedicated for nitrogen retention. However, the process has several limitations due to the concentration of chlorides in the water because the nitrogen ion in the water is exchanged with the chloride ion grafted onto the anion exchanger. Situations may occur in which nitrate concentrations are reduced and chloride excesses occur. Also, although anionites were designed to be selective, there is still a competitive action given by sulfate and bicarbonate ions. Groundwater generally has high concentrations of bicarbonate that, when competing with the nitrogen ion, lead to premature depletion of anionite exchange capacity.

On the other hand, when the exchange capacity is exhausted, the anionite mass must be regenerated and has significant consumption of regenerating brine, and the regeneration results in significant quantities of brine with high nitrogen content, quantities which in turn represent a heavy waste. managed. The process is relatively stable, but can only function fully automated because the concentration of nitrates in the effluent is not constant over a cycle but increases progressively as

the anionite exchange capacity decreases. The process is only applicable to low exceedances of nitrogen concentrations and requires permanently qualified operating personnel.

Reverse osmosis is a physical process that involves the passage of water through a semipermeable membrane that can retain almost the entire amount of salts in the water. The process takes place at pressures higher than the osmotic pressure. The process results in permeate (pure water) - between 65% and 80% of the influential and concentrated flow (20% -35%), regardless of the quality of the raw water. In general, reverse osmosis is applied only at partial flow, so that the mixture of the permeate with raw water that does not pass through the osmosis system results in a water that falls within the limits imposed by current legislation on nitrogen and does not require remineralization. The fundamental problem is the formation of concentrate, which, like the brine resulting from ion exchange, must be treated or managed properly. The process has a very high degree of automation, which makes it suitable in rural areas, without the need for a permanent operator with a high degree of qualification [1] [7].

Electrodialysis is a process that is not widely used. It is suitable for low water flows. In the water treatment process, electrodes are inserted into the volume of water and a direct or pulsating current is applied between the electrodes, leading to water electrodialysis. [6]

2.1 The main advantages and disadvantages of current technologies for reducing the concentration of nitrates

A summary of the main technologies used to reduce the amount of nitrates in water intended for human consumption, as well as their main advantages and disadvantages, are presented in the following table.

Table 2.1 Nitrates reduction technologies [6].

	Ion exchangers	**Reverse osmosis**	**Electrodialysis**	**Biological denitrification**	**Chemical denitrification**
Considered quality parameters that may influence the process	Sulfates, Iron, Manganese, Bicarbonates, Heavy metals, Organic matter	Turbidity, Iron, Manganese, Total hardness, Heavy metals, Organic matter	Turbidity, Iron, Manganese, Total Hardness, Heavy Metals	Temperature, pH, anoxic conditions	Temperature, pH
pretreatment	Pre-filtration PH adjustment	Pre-filtration	Pre-filtration	PH adjustment, anoxic conditions	PH adjustment
After-treatment	Pre-filtration PH adjustment	PH adjustment and remineralization	PH adjustment and remineralization	Filtration, disinfection	PH adjustment, iron removal
Residue	Brine	Concentrate	Concentrate	sludge	sludge
Process start time	Minutes	Minutes	Minutes	The initial start of the process – days/weeks; After starting the process - minutes;	Minutes
Amount of water after treatment	97%	85%	95%	Approx. 100%	-

	Ion exchangers	**Reverse osmosis**	**Electrodialysis**	**Biological denitrification**	**Chemical denitrification**
Benefits	High efficiency; Simple operation;	High efficiency; Simple operation	High efficiency	Relatively low costs; No consumption of chemical reagents	It does not produce residues such as reverse osmosis, ion exchange processes, or electrodialysis
Disadvantage	Water pretreatment is required; Automation required; High costs in case of waters with high mineralization; Necessary reagents for regeneration; The regeneration solution is difficult to manage;	Water pretreatment is needed; Automation required; High costs if all the water flow passes through the installation; Remineralization required; The result is concentrated, and difficult to manage;	Energy consuming process; Complex operation; The result is a concentrate that is difficult to manage;	Process dependent on temperature, alkalinity, pH, dissolved oxygen; Possible nitrite formation; Heavy process initiation; Additional carbon source required for low alkalinity waters;	Temperature and pH-dependent process; Possible nitrite formation; The process is used only for very low water flows.

3 Experimental set-up

The installation used for experiments consists of:

- Raw water basin;
- Submersible pump:
- Raw water distributor with the role of distributing the flow evenly in the 3 columns;
- 3 filter columns filled with different filter materials, each filter layer having a height of 1 m:
  - Sand filter;
  - Activated carbon filter;
  - Ceramic granule filter;
- Filtered water drainage pipes.

The scheme of the installation used is presented in the following figure:

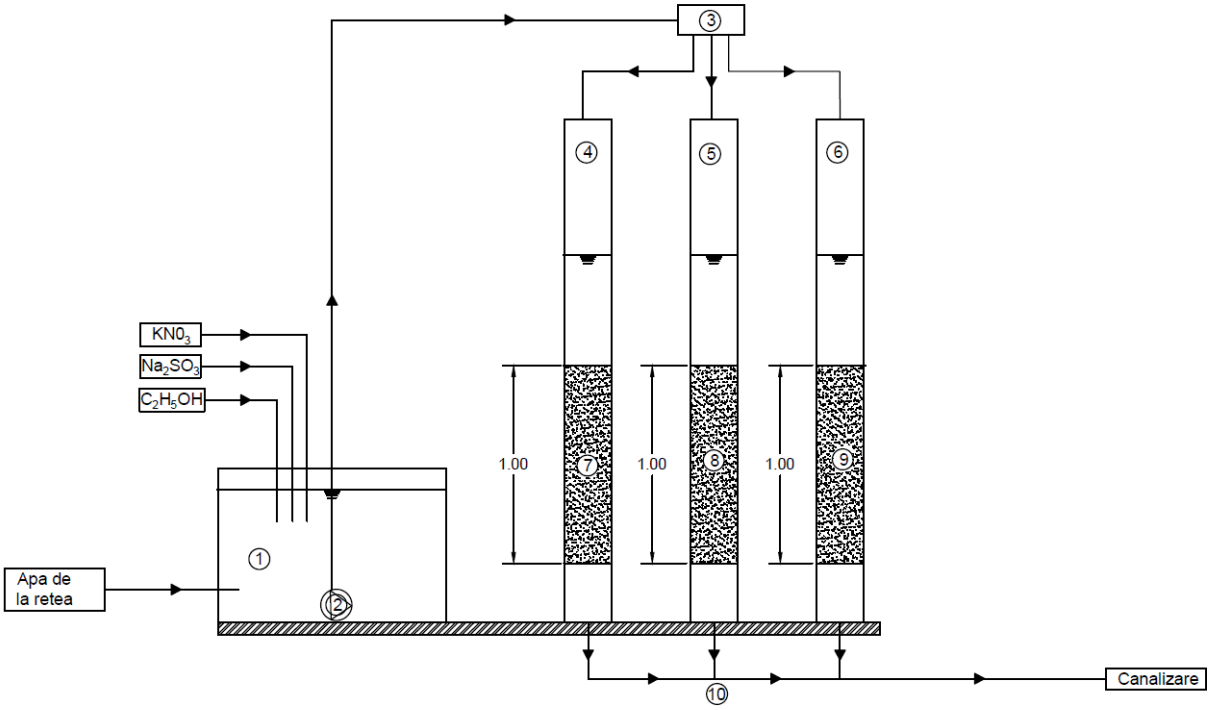

Figure 3.1. Experimental installation
1-Raw water tank, 2-Submersible pump, 3-Distributor, 4-Sand column, 5-Activated coal column, 6-Ceramic granule column, 7-Filter-sand layer, 8-Filter-activated carbon layer, 9-Layer filter-ceramic granules, 10-Drained filtered water.

4 Apparatus and instrumentation

The raw water used in the experimental determinations is represented by the water taaken from the hot water network of the Colentina laboratory complex. This water was chosen because, after checking the chlorine concentration in the water, it was in the range of 0 - 0.05 mg/l, a concentration that cannot negatively influence the development of biomass.

To achieve the desired concentration of nitrate, potassium nitrate (KNO_3) was added to the feed tank, the required amount of potassium nitrate being calculated in advance and verified by water analysis, after adding nitrate and dissolving it in water.

The external source of carbon needed for biomass development was provided by the addition of food ethyl alcohol (C_2H_5OH) from agricultural sources.

Orthophosphoric acid (H_3PO_4) was added to provide the required amount of phosphorus.

To reduce the amount of oxygen in the raw water, 10 mg of sodium sulfite was added to reduce 1 mg of oxygen dissolved in the water.

A submersible pump was used to supply the biofilter.

4.1 The main tools used in the experimental tests

4.1.1 Analytical balance

To prepare the raw water, it was necessary to add exact amounts of potassium nitrate and sodium sulfite. To dose the most accurate amount of substance and obtain a raw wat with the desired characteristics, a precision balance with internal calibration was used. It has a maximum capacity of 210 g and an accuracy of ± 0.2 mg. The balance is shown in the following figure.

Figure 4.1. Analytical balance.

4.1.2 HQ440D Multi-parameter

The HQ440D meter is a multi-parameter laboratory equipment with two input channels for simultaneous measurement of pH, dissolved oxygen (OD), and also temperature using sensors specially designed for these indicators.

Both the measuring device and the sensors are produced and marketed by Hach Lange.

The following figure shows the HQ440D measuring device.

Figure 4.2. HQ440D meter and Intellical sensors. Source: www.hach.com

In the experimental determinations, both for raw water and for filtered water, the indicators of interest were the pH and the concentration of dissolved oxygen in the water. Intellical sensors for measuring pH and dissolved oxygen concentration were used to determine them.

Intellical LDO101 is an optical digital sensor used to measure luminescent dissolved oxygen (LDO). The version used was a laboratory probe equipped with a temperature sensor.

Intellical PHC805 is a digital pH electrode with a built-in temperature sensor. This electrode is a glass electrode and is used to measure pH in laboratory applications.

The following images show the sensors used:

Figure 4.3. Intellical sensors - PHC805 - left. LDO101 - right.
Source: www.hach.com

4.1.3 Pipettes

For the accurate dosing of liquid reagents, glass pipettes with volumes of 1 ml, 5 ml, 10 ml, and 20 ml and a pipette with a variable volume of 0.2-1.0 ml were used.

The following images show the type of pipettes used.

Figure 4.4. glass pipettes –left; pipette with variable volume 0.2 - 1 ml - right.
Source: https://images.google.com

4.1.4 DR3900 spectrophotometer

The DR3900 spectrophotometer is manufactured and marketed by Hach Lange. It is intended for the analysis of water samples in the laboratory, using visible spectrum radiation (VIS) with reference beam technology with a wavelength in the range of 320 - 1100 nm.

Laboratory reagents specially designed for this purpose were used for the analysis. It was decided to use bar code kits consisting of ampoules containing the necessary reagents pre-dosed for a pre-defined measurement interval. With the help of RFID technology, the spectrophotometer can read the barcodes of the ampoules used and can identify the analyzed indicator, the measurement range, and the validity of the reagents, directly displaying the analyte concentration.

The reagents used are:

- Reagents for the determination of free chlorine by the DPD method (N, N-diethyl-p-phenylenediamine);
- Kit with barcode for nitrate 1 - 60 mg / l - LCK339;
- Barcode kit for nitrogen 22 - 155 mg / l - LCK340;

The following figures show the DR3900 test kits and spectrophotometer.

Figure 4.5. DR3900 spectrophotometer.

4.1.5 Others

Different laboratory instruments were used to collect samples, perform determinations such as the concentration of organic substances in water, and measure larger volumes of liquids, such as:

- Graduated cylinder with a volume of 100 ml;
- Erlenmeyer glass;
- Berzelius glass.

5 Experimental part

The experiments took place in two phases:

- Phase 1 - Development of denitrifying biomass;
- Phase 2 - Analysis of the efficiency of biofilters to reduce the concentration of nitrogen in the water.

The experimental protocol is similar in both phases. The difference between the two phases is represented by the volume of the container in which the raw water is stored (200 l in the first phase and 1000 l in the second phase) and by the concentrations of nitrates in the raw water (in phase 1 raw water was used with a concentration of 150 mg/l until the development of biomass, and during the testing of the efficiency of the installation, several concentrations of nitrates were used to evaluate the influence of the initial concentration of nitrates on the efficiency of the process).

The water from the hot water network of the Colentina laboratory complex was used to prepare the raw water. This water was used because, after its analysis, a low concentration of chlorine was determined, a concentration well below the concentration of water in the cold water installation.

After filling the raw water tank, the pH of the water and the amount of oxygen dissolved were checked. Because denitrifying bacteria use oxygen from the nitrate molecule in the respiration process, it was necessary to reduce the amount of dissolved oxygen in the water to less than 0.2 mg/l. Anhydrous sodium sulfite was used to achieve this concentration, the sodium sulfate/oxygen ratio being 10 to 1.

Potassium nitrate was used to achieve the desired concentration of nitrate.

During denitrification, for the good development and functioning of the biomass, it is necessary to ensure a C: N: P ratio of 100: 5: 1. Ethyl alcohol and orthophosphoric acid were used to achieve this ratio. To increase the nitrogen concentration by one milligram, for one liter of water, and to keep the C: N: P ratio of 100: 5: 1, it was necessary to add:

- 1.63 mg of potassium nitrate;
- 3.77 ml of ethyl alcohol;
- 0.09 ml phosphoric acid.

After homogenization, raw water samples were taken. These samples determined the values of the concentration of nitrate in the water, the amount of dissolved oxygen, the pH, and the concentration of organic substances in the raw water. If the results confirmed the preparation of raw water according to the calculations, the installation was started. The installation worked with a downward flow so that the water was pumped into the distributor, from the distributor, the columns were gravitationally fed and the water filtration was also gravitational. The filtered water was reintroduced into the raw water basin during the biomass development period and during the experimental tests, it was directed to the sewer, without re-entering the filtration system. After a while samples of filtered water were taken to determine the concentration of nitrates in the effluent of each filtered column, the pH of the filtered water, and the amount orgaof nic matter in the filtered water.

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5.1 Operation of biofilters in phase 1

Phase 1 had as its main objective the development of stable denitrifying biomass, capable of reducing the concentration of nitrate in raw water.

Although the time required for biomass development could be reduced by adding a biological preparation containing denitrifying bacteria, it was decided to grow naturally.

The nitrogen concentration of the prepared solution was 150 mg / l and the C: N: P ratio was 100: 5: 1.

The container in which the raw water was stored had a volume of 200 l.

The biofilter worked with recirculation to ensure the accumulation of biomass and prevent its washing out of the system. Every 3 days, the raw water used was discarded and replaced with a new solution, which had the same parameters for the concentrations of nitrogen, oxygen, carbon, and phosphorus.

Each biofilter operated at a constant flow rate of 20 l/h and a filtering speed of 2.54 m/h.

After about a month and a half, tests were performed on the raw and filtered water in each filter, and reductions in the nitrogen concentration of about 90% were observed.

5.2 Operation of biofilters in phase 2

The objective of the phase 2 operation of the biofilter was to test the filtration technology by treating solutions with different concentrations of nitrogen.

After the completion of phase 1 of the experiment, the experimental installation was modified, instead of the raw water tank (200 l) a new tank with a volume of 1000 l was installed. In this way, the maximum operating time of the installation without recirculation was increased. , requiring fewer interventions to supplement the amount of raw water.

The experimental determinations took place between 31.01.2021- 02.03.2021.

On 31.01.2021, after the completion of phase 1, a solution with a concentration of 150 mg/l of nitrate was prepared and the biofilter worked until 05.02.2021 using recirculation. The raw water has been refreshed, being replaced with a new solution every 3 days.

The day before the experimental tests, the water recirculation was stopped. The amount of raw water was filled in at 12 hours and a day later, after filling with raw water, experimental tests were performed on the installation. The tests consisted of taking water samples from each biofilter. Water samples were taken both from the effluent of the biofilters and different heights in its layer and the concentrations of nitrates and organic substances in the water were determined.

Water samples were taken every 3 hours. The filtered water was taken both from the outlet of the filter to determine the filtration efficiency and from the filter, layer to determine the distribution of the reduction efficiency in the filter layer.

The following tests were performed on both raw and filtered water taken from the filter outlet:

- Determination of pH;
- Determining the amount of nitrates using test kits;
- Determination of oxidability (CCO-Mn);

Apart from these determinations, the dissolved oxygen concentration was determined for the raw water to add sodium sulfite to reduce this concentration below the value of 0.2 mg/l.

Only the nitrate concentration was determined for the water samples taken from the filter layer.

After completion of the experimental tests, the cycle was repeated using a solution with a different concentration of nitrates.

The nitrate concentrations used in the experiment were 100 mg/l, 150 mg/l and 300 mg/l.

The following table shows the operating schedule of the pilot plant:

Table 5.1 Phase 2 development schedule - experimental testing.

	Sunday	Monday	Tuesday	Wednesday		Th.	Friday	Saturday	Saturday	Saturday
Week 1	Recirculation			Water Refreshing	Recirculation		No recirculat.	Tests	Raw water preparation	Recirculat.
Week 2	Recirculation			Water Refreshing	Recirculation		No recirculat.	Tests	Raw water preparation	Recirculat.
Week 3	Recirculation			Water Refreshing	Recirculation		No recirculat.	Tests	Raw water preparation	Recirculat.
Week 4	Recirculation		No recirculation	Tests	Water Refreshing	Recirculation				
Week 5	Recirculat.	No recirculat.	Tests	End of experimental stage						

6 Results obtained

The biofilters used are made of transparent PVC columns with an inner diameter of 100 mm and a height of 2.45 m. The filter layer is not placed on the entire height of the filter, it has a height of 1 m. The filter layer used was different for each biofilter. The filter materials used are:

- Granular activated carbon;
- Sand filter;
- Ceramic granules.

6.1 Experimental cycle 1

Experimental tests began a week after the completion of the biomass formation and development stage.

As the experimental tests could not be performed until the end of the week, it was decided that the installation should be operated by recirculating the water until one day before the tests were performed when the recirculation was stopped, the water is passed through the filter only once.

On the day of the test, the amount of raw water was filled to a volume of 1000 l. After that, raw water tests were performed to verify the correctness of the water preparation. After their validation, the installation was started. The filtered water was taken at 3 and 6 hours.

6.1.1 Raw water

The first test was performed with a concentration of nitrates in raw water identical to that used to initiate the process.

To obtain a water wh a nitrogen concentration equal to 150 mg/l, it was necessary to add 245 grams of potassium nitrate to 1000 l of water. To ensure the external source of carbon, a quantity of 282.5 ml of alcohol 96% of agricultural origin was added to the water. Orthophosphoric acid - 14 ml was also added to the water.

To reduce the amount of dissolved oxygen in the water below 0.2 mg/l, 280 g of sodium sulfite was added.

The characteristics of the raw water resulting from the laboratory determinations are presented in the following table:

Table 6.1 Raw water characteristics experimental cycle 1.

No.	Water volume (l)	Dissolved oxygen (mg/l)	nitrates (mg/l)	pH	Orgnaic matter (mg KMnO4/l)
1	1000	0.19	151	7.62	56.88
2	1000	0.19	148	7.62	56.88

6.1.2 Efficiency of biofilters in reducing the amount of nitrate dissolved in water

The following table shows the nitrogen concentration measured for the raw water and the water taken from the outlet of each biofilter. The water was taken 3 and 6 hours after the biofilter was put into operation.

Table 6.2 Nitrogen concentrations in filtered water - experimental cycle 1.

Biofilter service life	Raw water (mg/l)	Activated carbon filter (mg/l)	Ceramic granule filter (mg/l)	Sand filter (mg/l)
3 h	150	4.4	9.04	80.7
7 h		2.13	1.07	7.83

The calculated efficiency for each biofilter is presented in the following table:

Table 6.3 Calculated efficiency.

Biofilter service life	Activated carbon filter	Ceramic granule filter	Sand filter
3 h	97%	94%	46%
7 h	99%	99%	95%

It can be seen that, although the concentration of nitrogen resulting from the exit of water from each filter is below the maximum allowable limit according to the legislation in force for drinking water (50 mg/l) in 5 out of 6 samples, activated carbon filters and ceramic granules have yielded better than a sand filter.

In the case of the sand filter, the water resulting from the first cycle does not fall within the norms imposed by the legislation.

6.1.3 Distribution of the reduction of the nitrogen concentration inside the biofilters

The following figure shows the distribution of nitrogen concentration in the filter layers of the biofilter for water taken at the end of the filtration cycle (7 hours after startup of the biofilter).

The graphs showing the distribution of nitrate concentration in the filter layers of the biofilter for filtered water, taken at 3 hours are presented in the appendix.

To create these graphs, the values determined for the water samples taken from each filter layer were considered.

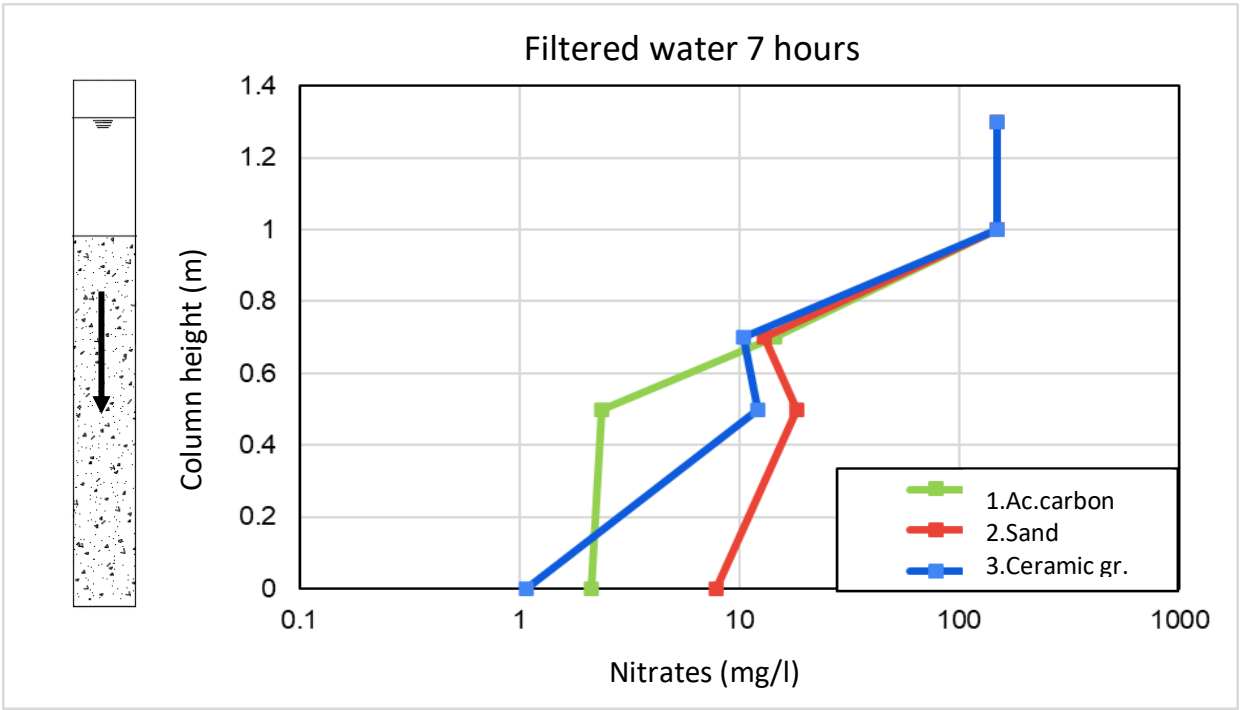

Figure 6.1. Distribution of the reduction of the nitrogen concentration in the filter layer - filtered water - 7 hours.

It can be seen that in the first 30 cm of the filter layer there is a reduction of the largest amount of nitrates in the raw water. The values of the nitrogen concentration determined for the filtered water taken from the first 30 cm of each filter layer as well as the reduction efficiency for each filter layer are presented in the following table:

Table 6.4 Efficiency of reducing the concentration of nitrogen in the filter layer - 1-0.7 m - week 1.

Biofilter service life	Raw water (mg/l)	Activated carbon filter (mg/l)	Efficiency (%)	Ceramic granule filter (mg/l)	Efficiency (%)	Sand filters (mg/l)	Efficiency (%)
3 h	150	6.7	96%	11.6	92%	77.6	48%
7 h	150	14.6	90%	10.4	93%	13.1	91%

It can be seen that the first layer is the most effective in reducing the concentration of nitrates, in 5 out of 6 samples, thus ensuring a reduction of over 90% of the influential amount of nitrates.

6.1.4 Oxidability of water

The oxidizability of raw water and filtered water was determined. The results obtained are presented in the following table.

Table 6.5 Water oxidability - experimental cycle 1.

Biofilter service life	Raw water (mg/l)	Activated carbon filter (mg/l)	Ceramic granule filter (mg/l)	Sand filter (mg/l)
3 h	56.88	63.2	75.84	72.68
7 h	56.88	63.2	69.52	79

A fluctuation of the oxidability value for the sampled water can be observed.

In the case of biofilters, the heat filter layer is made of activated carbon and sand, and the oxidability is increasing in both samples. In the case of the ceramic granule biofilter, the concentration of organic substances in the water increases in the first filtration cycle, following a slight decrease in the concentration in the second sample, but the value is above the oxidability value of the raw water. The variation of water oxidability for each filter is shown in the following graph.

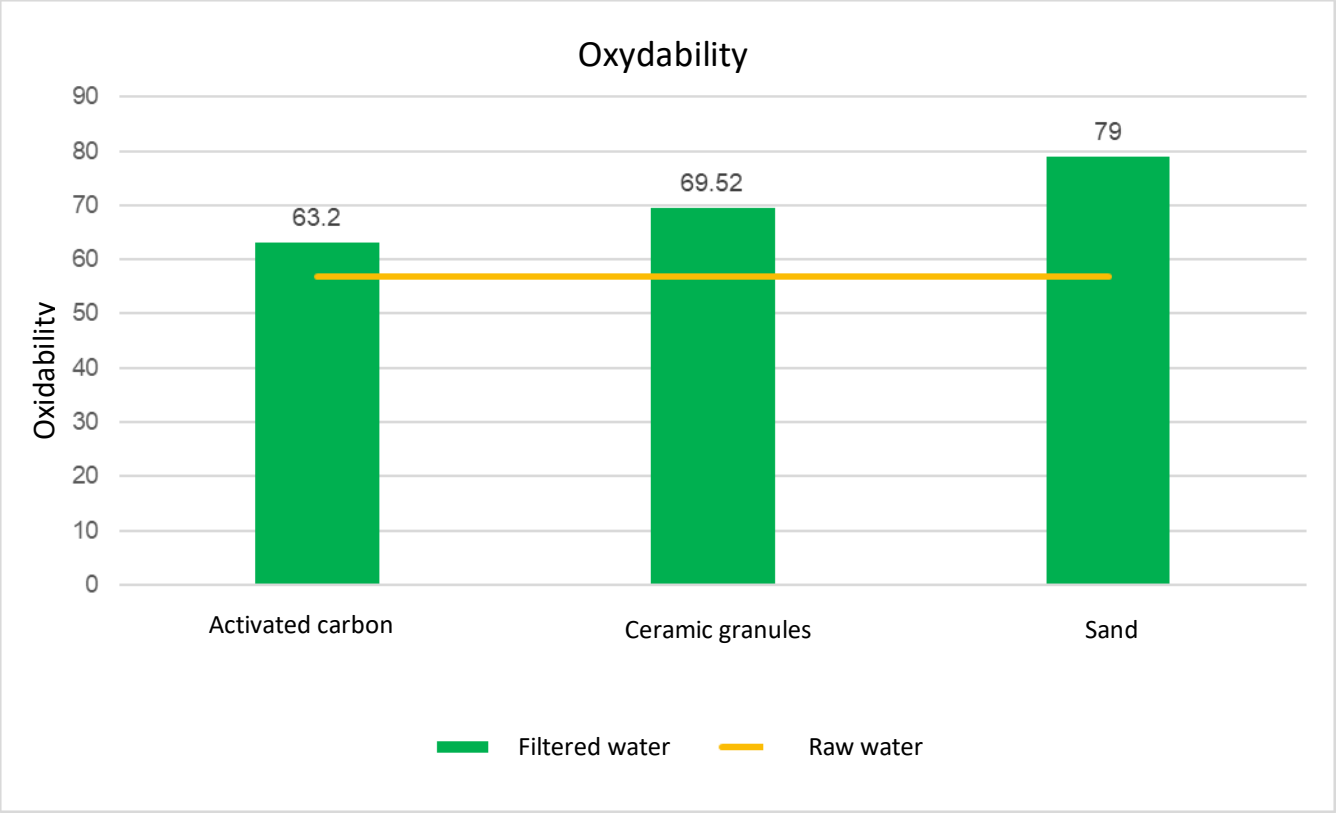

Figure 6.2. Oxidability variation - experimental cycle 1 - 7 hours.

6.2 Experimental cycle 2

As the experimental tests could not be performed until the end of the week, it was decided that the installation should be operated by recirculating the water until one day before the tests were performed when the recirculation was stopped, the water is passed through the filter only once.

On the day of the test, the amount of raw water was filled to a volume of 1000 l. After that, raw water tests were performed to verify the correctness of the water preparation. After their validation, the installation was started. The filtered water was taken at 3, 6, and 9 hours.

6.2.1 Raw water

For the second experimental test, the efficiency of the biofilter in reducing the nitrate concentration for raw water with a concentration of 100 mg/l was verified. To obtain a water with these characteristics it was necessary to add 164 g of potassium nitrate. To ensure the external source of carbon, a quantity of 200 ml of alcohol of 96% and agricultural origin was added to the water. Orthophosphoric acid - 9 ml was also added to the water.

To reduce the amount of dissolved oxygen in the water below 0.2 mg/l, 300 g of sodium sulfite was added.

The characteristics of the raw water resulting from the laboratory determinations are presented in the following table:

Table 6.6 Raw Water characteristics Week 2

No.	Water volume (l)	Dissolved oxygen (mg/l)	nitrates (mg/l)	pH	Orgnaic matter (mg KMnO4/l)
1	1000	0.2	101	8.2	63.2
2	1000	0.2	103	8.2	63.2

6.2.2 Efficiency of biofilters in reducing the amount of nitrate dissolved in water

The following table shows the nitrogen concentration measured for the raw water and the water taken from the outlet of each biofilter. The water was taken 3, 6, and, 9 hours after the commissioning of the biofilter.

Table 6.7 Nitrogen concentrations in filtered water - experimental cycle 2.

Biofilter service life	Raw water (mg/l)	Activated carbon filter (mg/l)	Ceramic granule filter (mg/l)	Sand filter (mg/l)
3 h	100	3.78	2.82	2.13
6 h		0.3	Under detection limit	Under detection limit
9 h		0.1	Under detection limit	Under detection limit

The calculated efficiency for each biofilter is presented in the following table:

Table 6.8 Calculated efficiency.2.

Biofilter service life	Activated carbon filter	Ceramic granule filter	Sand filter
3 h	96.22%	97.18%	97.87%
6 h	99.70%	SLD	SLD
9 h	99.90%	SLD	SLD

From the previous tables it can be seen that for all the water samples taken at the water outlet of each filter, the concentration of nitrates is below the maximum allowable limit according to the legislation in force for drinking water (50 mg / l). The filters have a better efficiency after 6 and 9 hours of biofilter operation, respectively, but their efficiency does not decrease below 96% even in the case of water taken 3 hours after starting the installation. Sand and ceramic granule filters perform better than activated carbon filters.

6.2.3 Distribution of the reduction of the nitrogen concentration inside the biofilters

The following figure shows the distribution of nitrogen concentration in the filter layers of the biofilter for water taken at the end of the filtration cycle (9 hours after commissioning of the biofilter).

The graphs showing the distribution of nitrogen concentration in the filter layers of the biofilter for filtered water, taken at 3 and 6 hours, respectively, are presented in the appendix.

To create these graphs, the values determined for the water samples taken from each filter layer were considered.

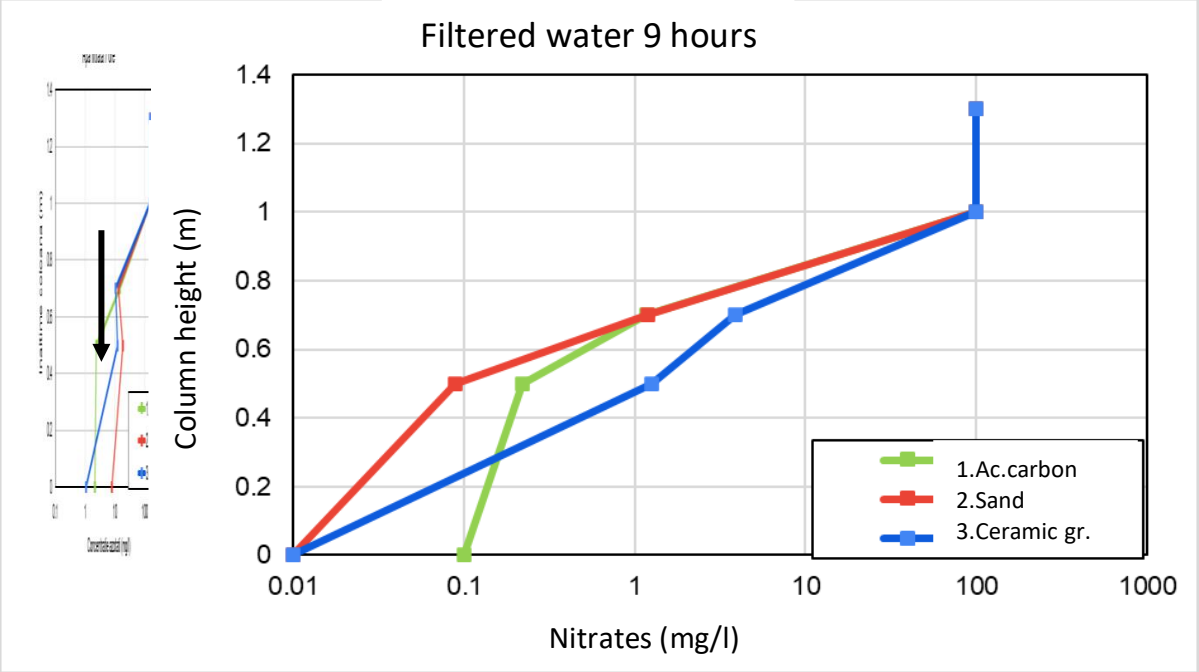

Figure 6.3. Distribution of the reduction of the nitrogen concentration in the filter layer - filtered water - 9 hours.

It can be seen that in the first 30 cm of the filter layer there is a reduction of the largest amount of nitrates in the raw water. The values of the nitrogen concentration determined for the filtered water taken from the first 30 cm of each filter layer as well as the reduction efficiency for each filter layer are presented in the following table.

Table 6.9 Efficiency of reducing the concentration of nitrogen in the filter layer - 1-0.7 m - experimental cycle 2.

Biofilter service life	Raw water (mg/l)	Activated carbon filter (mg/l)	Efficiency (%)	Ceramic granule filter (mg/l)	Efficiency (%)	Sand filters (mg/l)	Efficiency (%)
3 h	100	9.14	90.86%	10.55	89.45%	3.98	96.02%
6 h	100	0.4	99.60%	2.66	97.34%	2.46	97.54%
9 h	100	1.18	98.82%	3.87	96.13%	0.151	99.85%

It can be seen that the first layer is the most effective in reducing the concentration of nitrates, with more than 90% of the amount of nitrate in the water being reduced in the first 30 cm of each filter.

6.2.4 Oxidability of water

The oxidizability of raw water and filtered water was determined. The results obtained are presented in the following table.

Table 6.10 Water oxidability - experimental cycle 2.

Biofilter service life	Raw water (mg/l)	Activated carbon filter (mg/l)	Ceramic granule filter (mg/l)	Sand filter (mg/l)
3 h	63.2	53.72	56.88	37.92
6 h	63.2	63.2	44.24	69.52
9 h	63.2	116.92	85.32	142.2

There is a decrease in oxidizability for water taken after the first treatment cycle between 10 and 40% of the initial value. In the case of water taken at 6 and 9 hours, respectively, the amount of organic substances in the water begins to increase, reaching in the case of water taken at 9 hours even 125% of the initial value for the sand filter.

The following graph shows the variation of oxidizability for filtered water.

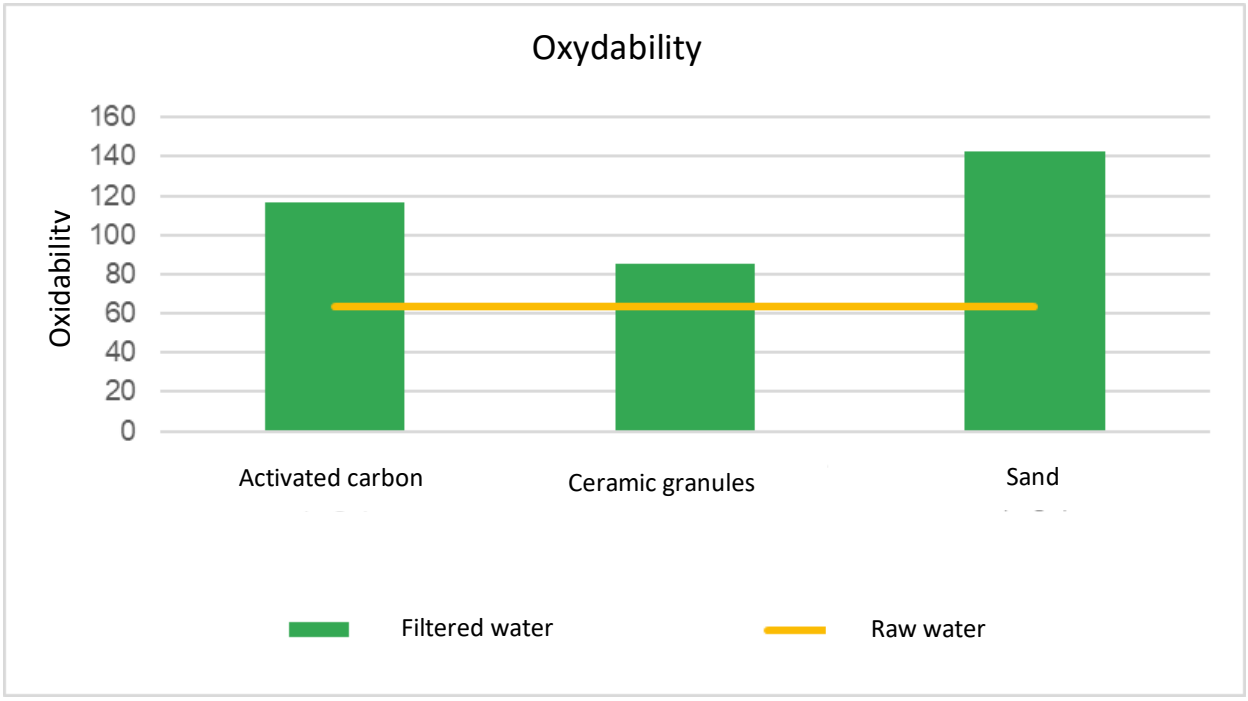

Figure 6.4. Oxidability variation - experimental cycle 2 - 9 hours.

6.3 Experimental cycle 3

For the 3rd attempt, raw water with a very high concentration of nitrates (300 mg/l) was prepared. Usually, water sources containing concentrations higher than 250 mg / l of nitrates are not used as water sources to supply the population, because the treatment processes are very expensive, being more efficient to use another water source if it is possible. The experimental protocol used was the same as in previous tests.

6.3.1 Raw water

For the third experimental test, it was verified the efficiency of the bio-filter in reducing a very high concentration of nitrates at 300 mg/l. To obtain water with these characteristics, it was necessary to add 491 g of potassium nitrate. To ensure the external source of carbon, a quantity of 665 ml of alcohol 96% of agricultural origin was added to the water. Also, orthophosphoric acid was added to the water – 28 ml. To reduce the amount of dissolved oxygen in the water below the concentration of 0.2 mg / l, 300 g of sodium sulfite were added. The characteristics of the raw water resulting from the laboratory determinations are presented in the following table:

Table 6.11 Raw water characteristics experimental cycle 3.

No.	Water volume (l)	Dissolved oxygen (mg/l)	nitrates (mg/l)	pH	Orgnaic matter (mg KMnO4/l)
1	1000	0.18	296	7.49	97.96
2	1000	0.18	302	7.49	97.96

6.3.2 Efficiency of biofilters in reducing the amount of nitrate dissolved in water

The following table is presenting the concentration of nitrate measured for raw water and water taken from the exit from each bio-filter. The water was taken 3, 6, and 9 hours after the commissioning of the bio-filter.

Table 6.12 Nitrogen concentrations in filtered water - experimental cycle 3.

Biofilter service life	Raw water (mg/l)	Activated carbon filter (mg/l)	Ceramic granule filter (mg/l)	Sand filter (mg/l)
3 h	300	0.87	6.21	24.74
6 h		0.23	11.8	2.25
9 h		0.864	0.653	0.811

The calculated efficiency for each bio-filter is presented in the following table:

Table 6.13 Calculated efficiency – experimental cycle 3.

Biofilter service life	Activated carbon filter	Ceramic granule filter	Sand filter
3 h	99.71%	97.93%	91.75%
6 h	99.92%	96.07%	99.25%
9 h	99.71%	99.78%	99.73%

It can be seen that for all the water samples taken at the exit of the water from each filter, the concentration of nitrates is below the maximum allowable limit according to the legislation in force for drinking water (50 mg/ l). The filters have a better efficiency after 6, respectively 9 hours of operation of the bio-filter, but their efficiency does not fall below 96% even in the case of water taken 3 hours after starting the installation. Activated charcoal filters and ceramic granules have a better yield than the sand filter.

6.3.3 Distribution of the reduction of the nitrogen concentration inside the biofilters

The following figure shows the distribution of the concentration of nitrates in the filter layers of the bio-filter for the water taken at the end of the filtration cycle (9 hours after the commissioning of the bio-filter). The graphs showing the distribution of the concentration of nitrates in the filter layers of the bio-filter for filtered water, taken at 3 and 6 hours respectively, are presented in the annex. In order to make these graphs, the determined values for the water samples taken from each filter layer were considered

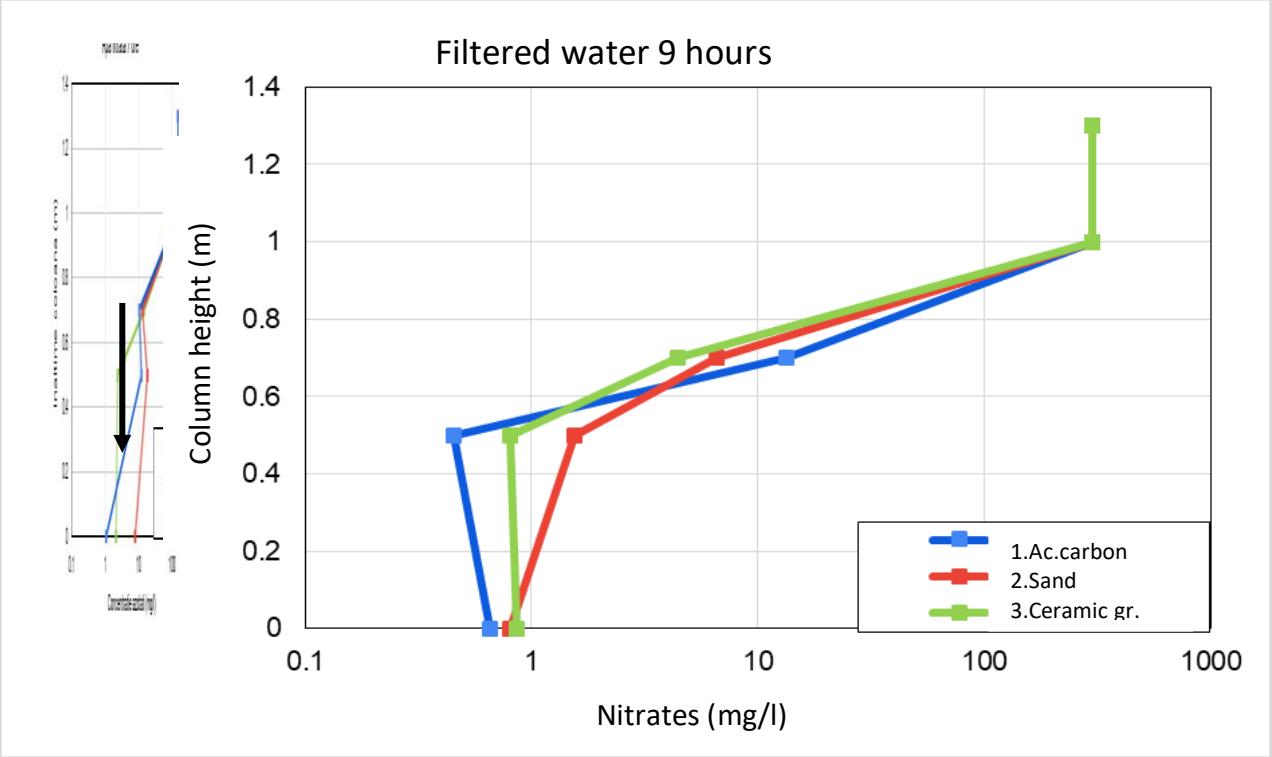

Figure 6.5. Distribution of the reduction of the nitrogen concentration in the filter layer - filtered water - 9 hours.

It can be seen that in the first 30 cm of the filter layer, the reduction of the largest amount of nitrates in the raw water takes place. The values of the nitrate concentration determined for the filtered water taken from the first 30 cm of each filter layer as well as the reduction efficiency for each filter layer are presented in the following table:

Table 6.14 Efficiency of reducing the concentration of nitrogen in the filter layer - 1-0.7 m - experimental cycle 3.

Biofilter service life	Raw water (mg/l)	Activated carbon filter (mg/l)	Efficiency (%)	Ceramic granule filter (mg/l)	Efficiency (%)	Sand filters (mg/l)	Efficiency (%)
3 h	300	0.64	99.79%	7.39	97.54%	39.74	86.75%
7 h	300	3.42	98.86%	61.3	79.57%	4.86	98.38%
9 h	300	4.42	98.53%	13.4	95.53%	0.718	99.76%

It can be seen that the first layer is the most effective in reducing the concentration of nitrates, in 8 out of 9 samples, the value of the concentration of nitrates in the water taken after the first 30 cm of the bio-filter was below the concentration allowed by the legislation in force.

6.3.4 Oxidability of water

The oxidation of raw water and filtered water was determined. The obtained results are presented in the following table.

Table 6.15 Water oxidability - experimental cycle 3.

Biofilter service life	Raw water (mg/l)	Activated carbon filter (mg/l)	Ceramic granule filter (mg/l)	Sand filter (mg/l)
3 h	63.2	74.26	74.26	105.86
6 h	63.2	47.4	53.72	126.4
9 h	63.2	104.28	45.82	47.4

A fluctuation in the oxidation value for the sampled water can be observed. In the case of bio-filter with activated charcoal, the concentration of organic substances shows a decrease in the first two filtration cycles, then increasing a higher value than the initial one. The bio-filter of ceramic granules shows a constant decrease in toxicity for filtered water and the sand filter shows an increase in toxicity in the first two filtration cycles, this increase is followed by a decrease in the oxidation value below the initial value in the third filtration cycle. The following graph presents the variation of oxidation for filtered water, at the end of the filtration cycle (9 hours after the commissioning of the bio-filter). The graphs showing the variation of the oxidation of the filtered water, taken at 3 and 6 hours respectively, are presented in the annexes.

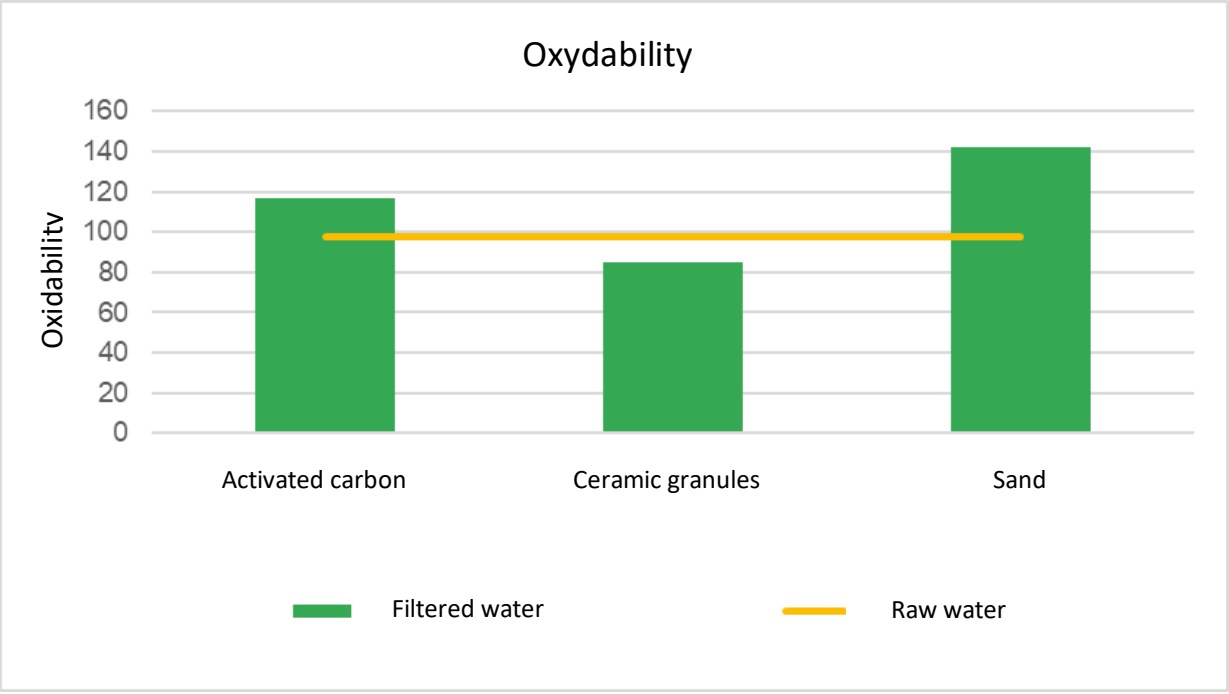

Figure 6.6. Oxidability variation - experimental cycle 2 - 9 hours.

6.4 Experimental cycle 4

As an increase in oxidizability was observed for the treated water, an attempt was made to reduce the amount of external carbon added. For this, only 10% of the amount of alcohol required for the proper functioning of biological denitrification was added, according to the literature.

To perform this test, water with nitrates concentration equal to 150 mg/l was prepared.

The experimental protocol used was the same but only one filtered water sample was taken, at 9 h from the start of the installation.

6.4.1 Raw water

For the fourth experimental test, the efficiency of the biofilter in reducing the amount of nitrates was verified, in the case of a reduced amount of carbon (10%). To obtain water with these characteristics it was necessary to add 245 g of potassium nitrate. To ensure the external source of carbon, a quantity of 28 ml of alcohol 96% of agricultural origin was added to the water. Orthophosphoric acid - 14 ml was also added to the water.

To reduce the amount of dissolved oxygen in the water below 0.2 mg / l, 300 g of sodium sulfite was added.

The characteristics of the raw water resulting from the laboratory determinations are presented in the following table:

Table 6.16 Raw water characteristics experimental cycle 4.

No.	Water volume (l)	Dissolved oxygen (mg/l)	nitrates (mg/l)	pH	Orgnaic matter (mg KMnO4/l)
1	1000	0.18	150	7.62	8.37
2	1000	0.18	151	7,62	8.37

6.4.2 Efficiency of biofilters in reducing the amount of nitrate dissolved in water

The following table shows the nitrogen concentration measured for the raw water and the water taken from the outlet of each biofilter. The water was taken 9 hours after the startup of the biofilter.

Table 6.17 Nitrogen concentrations in filtered water - experimental cycle 3.

Biofilter service life	Raw water (mg/l)	Activated carbon filter (mg/l)	Ceramic granule filter (mg/l)	Sand filter (mg/l)
9 h	150	0.24	54.1	77.1

The calculated efficiency for each biofilter is presented in the following table:

Table 6.18 Calculated efficiency – experimental cycle 3.

Biofilter service life	Activated carbon filter	Ceramic granule filter	Sand filter
9 h	99.84%	63.93%	48.60%

There is a decrease in the efficiency of reducing the amount of nitrates in the water in case of reducing the amount of external carbon added. It can be seen that sand filters and ceramic granules have suffered the most in the case of deprivation of the external carbon source. In the case of activated carbon biofilter, it is observed that it had a good efficiency in reducing nitrogen in water (99.84%).

6.4.3 Distribution of the reduction of the nitrogen concentration inside the biofilters

The following figures show the efficiency of reducing the concentration of nitrates in each filter layer.

In order to make these graphs, the values obtained for the water samples taken from the filter layer were considered.

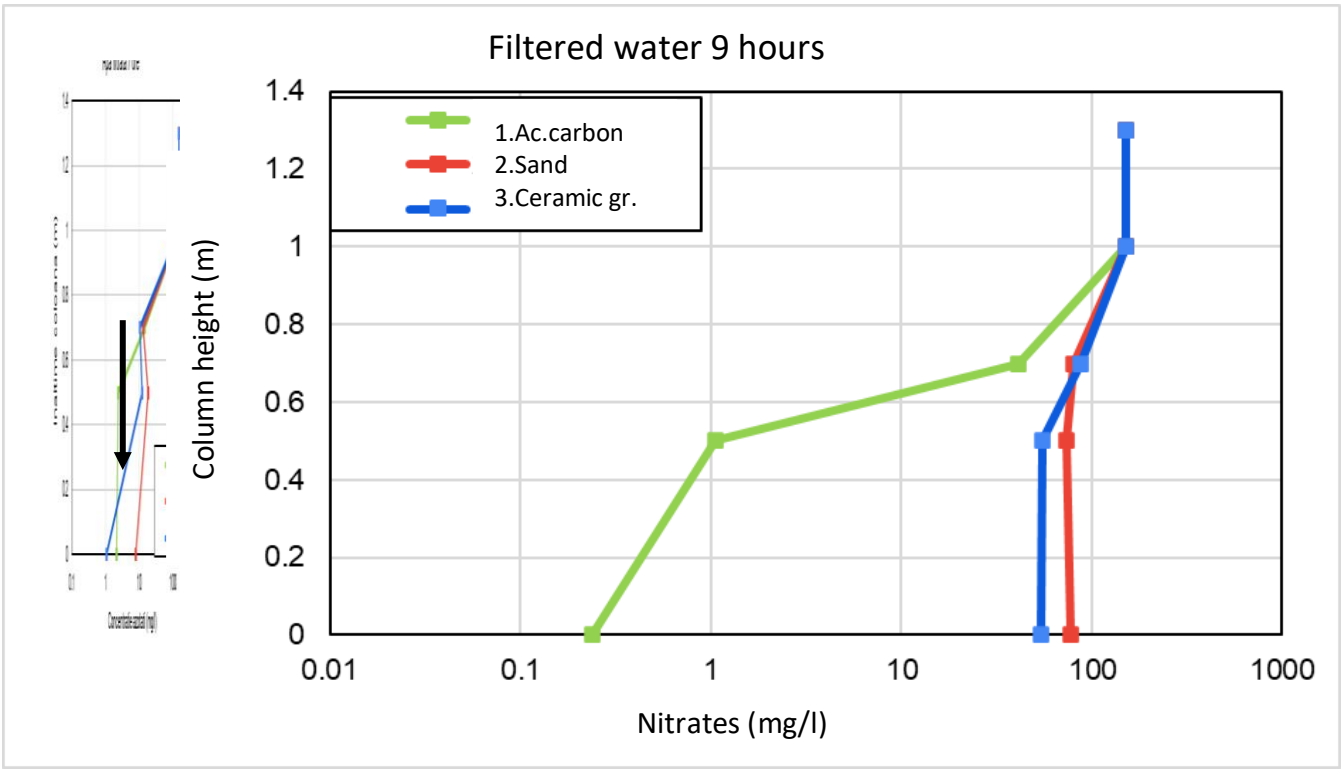

Figure 6.7. . Distribution of the reduction of the nitrogen concentration in the filter layer.

The values of the nitrogen concentration determined for the filtered water taken from the first 30 cm of each filter layer as well as the reduction efficiency for each filter layer are presented in the following table:

Table 6.19 Efficiency of reducing the concentration of nitrogen in the filter layer - 1-0.7 m - experimental cycle 4.

Biofilter service life	Raw water (mg/l)	Activated carbon filter (mg/l)	Efficiency (%)	Ceramic granule filter (mg/l)	Efficiency (%)	Sand filters (mg/l)	Efficiency (%)
9 h	150	41.3	72.47%	88	41.33%	80.8	46.13%

It can be seen that the first layer is the most effective in reducing the concentration of nitrates.

6.4.4 Oxidability of water

The oxidizability of raw water and filtered water was determined. The results obtained are presented in the following table.

Table 6.20 Water oxidability - experimental cycle 4.

Biofilter service life	Raw water (mg/l)	Activated carbon filter (mg/l)	Ceramic granule filter (mg/l)	Sand filter (mg/l)
9 h	37.92	11.16	7.69	6.98

The following graph shows the variation of oxidizability for filtered water.

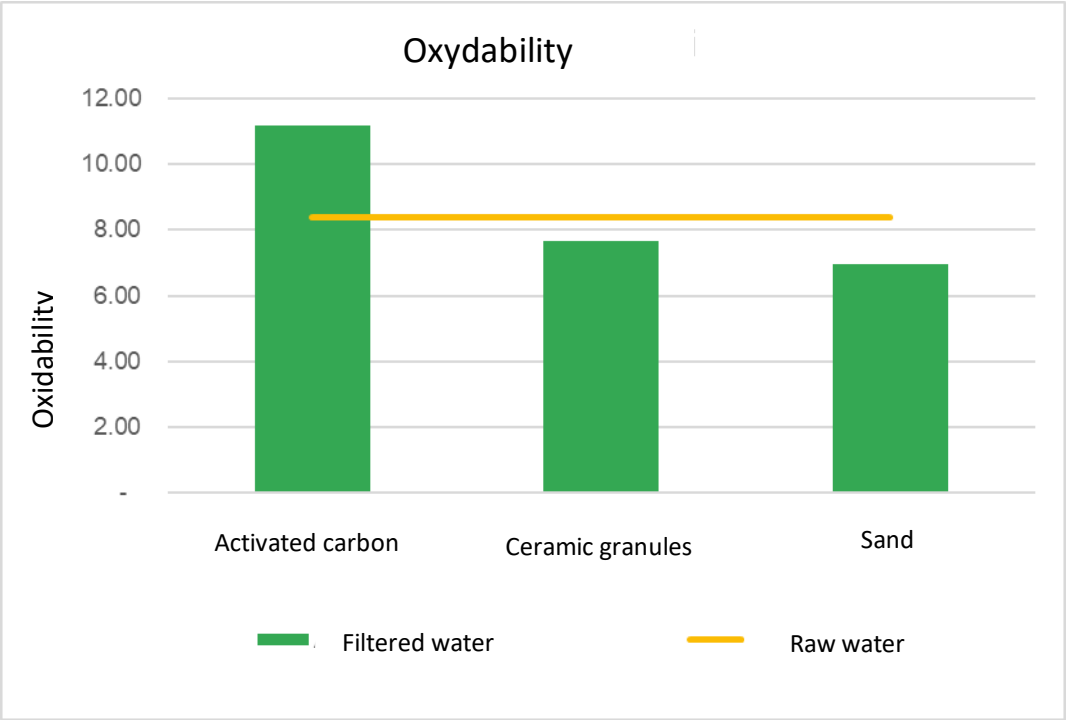

Figure 6.8. Oxidability variation - experimental cycle 4.

There is a decrease in the value of oxidizability for biofilters in which the reduction of the amount of nitrates did not have high efficiency. In the case of the biofilter whose filter layer is represented by activated carbon, which had a very good efficiency in reducing the concentration of nitrates, an increase in the oxidability value can be observed by approximately 33%.

6.5 Experimental cycle 5

The purpose of the fifth test was to determine the effectiveness of reducing the amount of nitrates for a shorter retention time. To perform this experiment, the pumped water flow in the pilot plant was doubled, thus doubling the filtration speed to 5.08 m/h. The retention time was thus reduced by half, from 23.6 minutes to 11.8 minutes.

Water with a nitrogen concentration equal to 150 mg/l was prepared for this test, the experiment took place under the same conditions as the previous ones. Only one filtered water sample was taken, 9 hours after starting the installation.

6.5.1 Raw water

For the fifth experimental test, the efficiency of the biofilter in reducing the amount of nitrates was verified for water with a nitrogen concentration equal to 150 mg/l. To obtain these characteristics it was necessary to add 245 g of potassium nitrate. To ensure the external source of carbon, a quantity of 282.5 ml of alcohol 96% of agricultural origin was added to the water. Orthophosphoric acid - 14 ml was also added to the water.

To reduce the amount of dissolved oxygen in the water below 0.2 mg/l, 300 g of sodium sulfite was added.

The characteristics of the raw water resulting from the laboratory determinations are presented in the following table:

Table 6.21 Raw water characteristics experimental cycle 5.

No.	Water volume (l)	Dissolved oxygen (mg/l)	nitrates (mg/l)	pH	Orgnaic matter (mg KMnO4/l)
1	1000	0.22	150	7.44	39.5
2	1000	0.20	151	7,44	39.5

6.5.2 Efficiency of biofilters in reducing the amount of nitrate dissolved in water

The following table shows the nitrogen concentration measured for the raw water and the water taken from the outlet of each biofilter. The water was taken 9 hours after the commissioning of the biofilter.

Table 6.22 Nitrogen concentrations in filtered water - experimental cycle 3.

Biofilter service life	Raw water (mg/l)	Activated carbon filter (mg/l)	Ceramic granule filter (mg/l)	Sand filter (mg/l)
9 h	150	SLD	0.387	SLD

The calculated efficiency for each biofilter is presented in the following table:

Table 6.23 Calculated efficiency – experimental cycle 3.

Biofilter service life	Activated carbon filter	Ceramic granule filter	Sand filter
9 h	UDL	99.74%	UDL

Biological denitrification did not suffer due to the increase of the filtration speed, this having results comparable to those obtained in the case of the speed of 2.54 m / h. It is observed that each filter reduced more than 99.7% of the amount of nitrate influence.

6.5.3 Distribution of the reduction of the nitrogen concentration inside the biofilters

The following figures show the efficiency of reducing the concentration of nitrates in each filter layer.

In order to make these graphs, the values obtained for the water samples taken from the filter layers were considered.

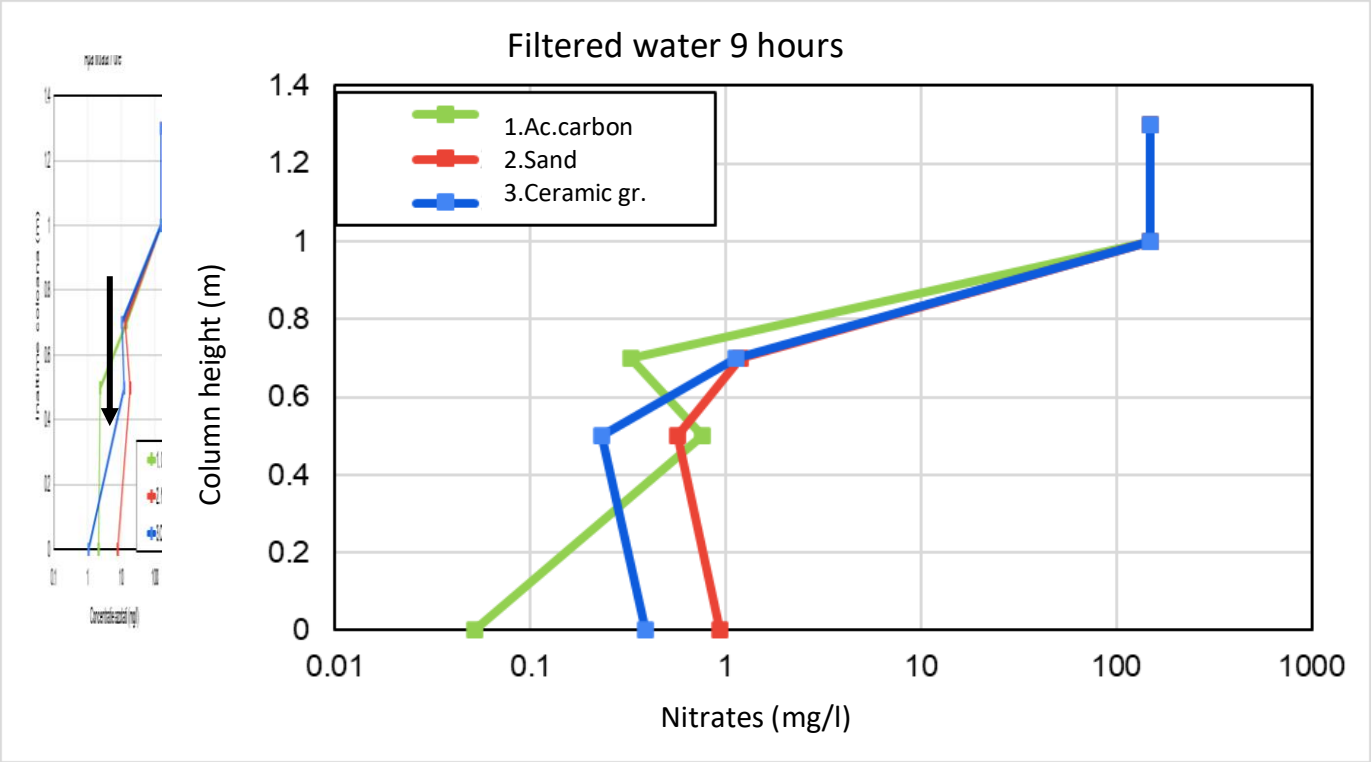

Figure 6.9. . Distribution of the reduction of the nitrogen concentration in the filter layer – 9 h.

As the graph was made only for the water samples taken from the filter layer, the reduction of the nitrogen concentration in the first 30 cm of the biofilter is not highlighted. These can be found in the following table:

Table 6.24 Efficiency of reducing the concentration of nitrogen in the filter layer - 1-0.7 m - experimental cycle 5.

Biofilter service life	Raw water (mg/l)	Activated carbon filter (mg/l)	Efficiency (%)	Ceramic granule filter (mg/l)	Efficiency (%)	Sand filters (mg/l)	Efficiency (%)
9 h	150	0.325	99.78%	1.12	99.25%	1.18	99.21%

It can be seen that the first layer is the most effective in reducing the concentration of nitrates for each biofilter, which reduces more than 99% of the influential amount of nitrate in the water.

6.5.4 Oxidability of water

The oxidizability of raw water and filtered water was determined. The results obtained are presented in the following table.

Table 6.25 Water oxidability - experimental cycle 5.

Biofilter service life	Raw water (mg/l)	Activated carbon filter (mg/l)	Ceramic granule filter (mg/l)	Sand filter (mg/l)
9 h	39.5	72.68	37.92	63.2

The following graph shows the variation of oxidizability for filtered water.

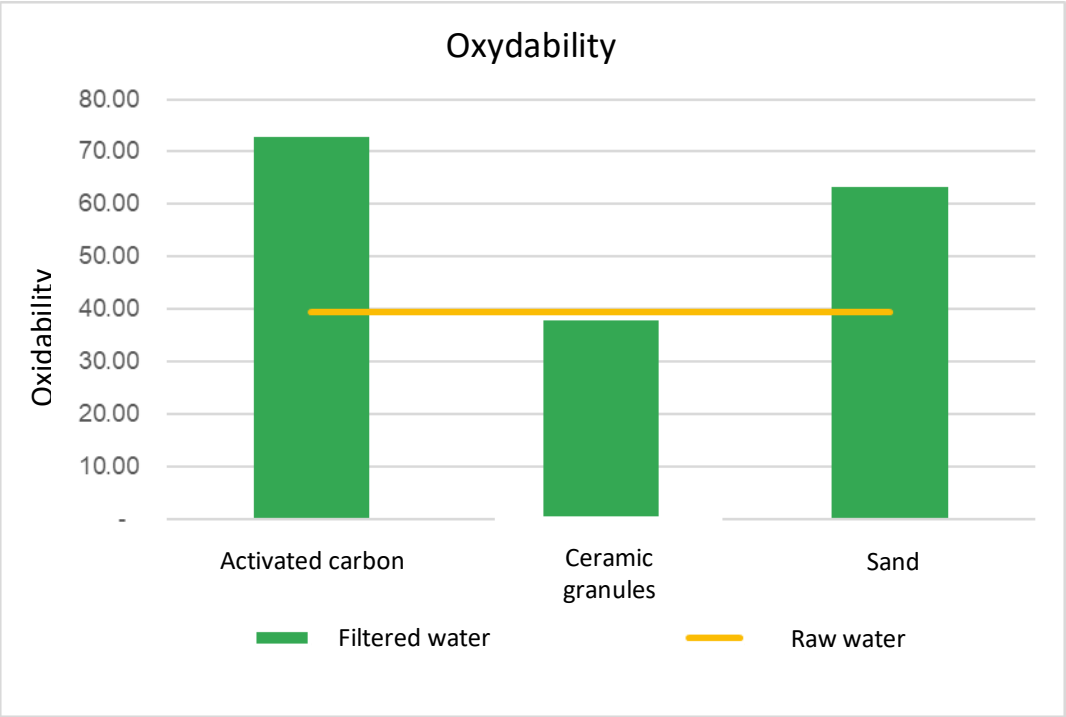

figure 6.10. Oxidability variation - experimental cycle 4.

There is a decrease in the oxidability value for the biofilter whose filter layer is made of ceramic granules. For the other two filters, the increase in oxidability is high, with 60% for the sand filter and 84% for the activated carbon filter.

7 Conclusions

A pilot biological denitrification plant was installed during the experimental tests. It consisted of 3 biofilters, filled with different filter materials: sand, ceramic granules, and activated carbon.

The experiment took place in 2 stages:

Stage 1 - Development of denitrifying biomass, its main objective was the development of stable denitrifying biomass, capable of reducing the concentration of nitrate in raw water. The option of developing biomass naturally was chosen, without the addition of any biological preparation. The time required for biomass formation was 1 month and a half.

Step 2 - Analysis of the efficiency of the biofilter to reduce the concentration of nitrates in the water for different concentrations. The experimental tests took place between 05.02.2021-02.03.2021.

The objective of the phase 2 operation of the biofilter was to test the filtration technology by treating solutions with different concentrations of nitrogen.

The tests took place weekly. One day before each experimental test, water recirculation was stopped. The amount of raw water was filled in at 12 hours and a day later, after filling with raw water, experimental tests were performed on the installation. The tests consisted of taking water samples from each biofilter, both from the biofilter effluent and from its layer, and determining the concentrations of nitrates and organic substances in the water.

Water samples were taken every 3 hours. The following tests were performed on both raw and filtered water:

- pH measurement;
- Determination of nitrate concentration using a DR 3900 photometer and Hach-Lange test kits;
- Determination of oxidability (CCO-Mn);

Apart from these determinations, the dissolved oxygen concentration was determined for the raw water to add sodium sulfite to reduce this concentration below the value of 0.2 mg / l.

For the water samples taken from the filter layer, only the nitrogen concentration in the water was determined.

The raw water concentrations for which the tests were performed are 100, 150, and 300 mg/l. For concentrations of 100 and 300 mg / l, filtered water from 3 filtration cycles (3, 6, and 9 hours) was analyzed.

The following table shows the results obtained in the experimental test for biological denitrification.

Table 7.1 Results obtained - reduction of nitrate concentrations.

Experimental cycle	Sub-cycle	Nitrates (mg/l)				Efficiency (%)		
		Raw water	Filtered water					
			Activated carbon filter	Ceramic granules filter	Sand filter	Activated carbon filter	Ceramic granules filter	Sand filter
1	**1** - 3 h	150	4.4	9.04	80.7	97.07%	93.97%	46.20%
	2 - 6 h		2.13	1.07	7.83	98.58%	99.29%	94.78%
2	**1** - 3 h	100	3.78	0.1	2.13	96.22%	99.90%	97.87%
	2 - 6 h		0.3	SLD*	SLD*	99.70%	99.99%	99.99%
	3 - 9 h		0.1	SLD*	SLD*	99.90%	99.99%	99.99%

Experimental cycle	Sub-cycle	Nitrates (mg/l)				Efficiency (%)		
		Raw water	Filtered water					
			Activated carbon filter	Ceramic granules filter	Sand filter	Activated carbon filter	Ceramic granules filter	Sand filter
3	**1** - 3 h	300	0.87	6.21	24.74	99.71%	97.93%	91.75%
	2 - 6 h		0.23	11.8	2.25	99.92%	96.07%	99.25%
	3 - 9 h		0.864	0.653	0.811	99.71%	99.78%	99.73%
4	**1** - 9 h	150	0.24	54.1	77.1	99.84%	63.93%	48.60%
5	**1** - 9 h	150	SLD	0.387	SLD*	99.99%	99.74%	99.99%
Minimum efficiency (%)						**96.22%**	**63.93%**	**46.20%**
Medium efficiency (%)						**99.06%**	**95.06%**	**87.82%**
Maximum efficiency (%)						**99.99%**	**99.99%**	**99.99%**

* - The concentration of nitrates was below the limit of detection of the method used.

At the concentration of 150 mg / l, water from 2 filtration cycles (3 and 6 hours) was analyzed, using the same conditions as for the other concentrations. Also for this concentration, two more tests were performed:

- Denitrification efficiency in case of reducing the amount of organic carbon in the water - 1 filtration cycle;
- Denitrification efficiency in case of doubling the filtration speed - 1 filtration cycle.

The obtained results highlighted the efficient use of biological denitrification. Thus, for all concentrations of nitrogen used, under normal operating conditions of biofilters, they reduced the concentration of nitrogen in the water to values below the limits imposed by current legislation (50 mg/l) for most samples (23 of 24).

Because the aim was to test the ability to reduce nitrogen concentrations using biological processes, two tests were performed to verify the ability to treat under unusual conditions. Thus, an attempt was made to reduce the amount of external carbon added in the process by 90%, in which case the reduction of nitrates took place in each filter, but the concentration of nitrates was below the limits imposed by law only for water treated in coal biofilter.

In the case of halving the retention time of the biofilters (experimental cycle no. 5), all 3 filters had very good results in reducing the amount of nitrates in the water.

After analyzing the results, it can be seen that all 3 biofilters are effective in reducing the concentration of nitrates in the water. However, the activated carbon filter was the only filter that reduced the concentration of nitrates below the level required by law in all experimental cycles, including cycle no. 4, which involved reducing the amount of nutrients.

Sand and granular ceramic biofilters have reduced the concentration of nitrates in filtered water with an efficiency of over 90% for all experimental cycles, except cycle no. 4, in which their efficiency decreased below 65% and the concentration of nitrates in the resulting water was above the limit value imposed by legislation. This results in a lower sensitivity of the biomass attached to the activated carbon filter as opposed to the other two filter media analyzed, which have shown a higher sensitivity of the biomass attached to the decrease in the amount of nutrients.

The following graph shows the nitrogen reduction efficiency of each biofilter at the end of each experimental cycle. For each filtration cycle, the normal alcohol concentration used to prepare the raw water in mg / l is shown.

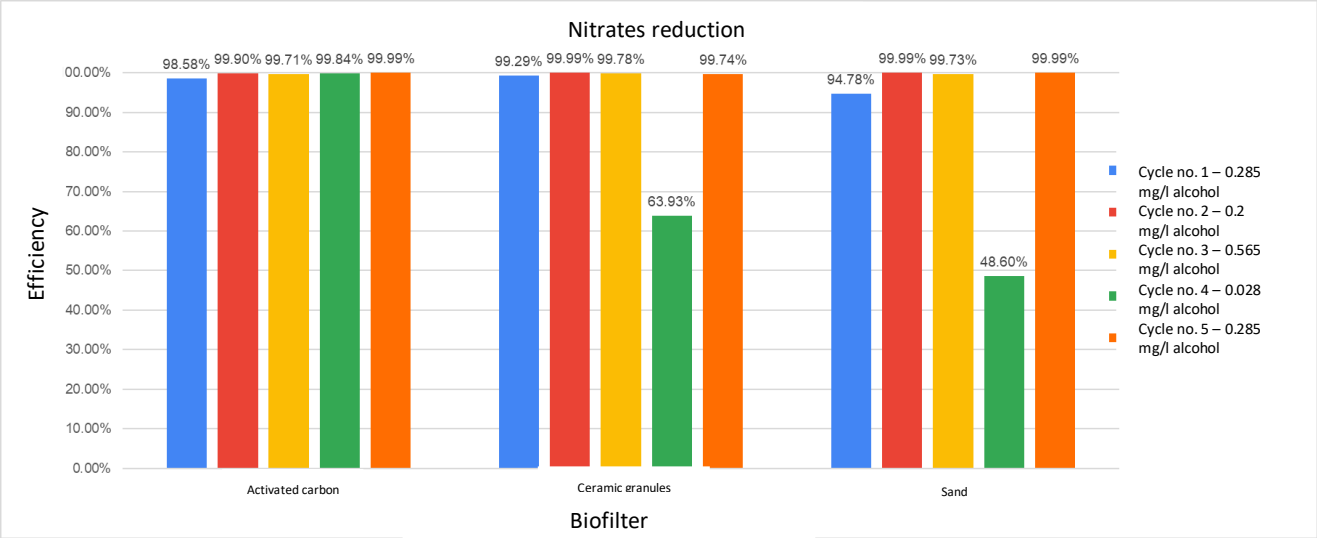

Figure 7.1. Nitrogen reduction efficiency.

The following table presents the results obtained in the experimental tests for the oxidability of raw water and filtered water, respectively. The oxidability of the water was determined by the water from the biofilter effluent.

Table 7.2 Results obtained - Oxidability of water.

Experimental cycle	Sub-cycle	Oxidability (mg $KMnO_4$/l)			
		Raw water	Filtered water		
			Activated carbon filter	Ceramic granules filter	Sand filter
1	1 - 3 h	56.88	63.2	75.84	72.68
	2 - 6 h		63.2	69.52	79
2	1 - 3 h	63.2	53.72	37.92	37.92
	2 - 6 h		63.2	69.52	69.52
	3 - 9 h		116.92	142.2	142.2
3	1 - 3 h	97.96	74.26	74.26	105.86
	2 - 6 h		47.4	53.72	126.4
	3 - 9 h		104.28	45.82	47.4
4	1 - 9 h	37.92	50.56	34.76	31.6
5	1 - 9 h	39.5	72.68	37.92	63.2

The amount of organic matter present in filtered water was higher than in raw water for most samples, which implies the need for a post-treatment step to eliminate it, otherwise, there is a risk of THM formation in treated water, potentially carcinogenic compounds.

This increase in the oxidizability of filtered water has been observed in other similar experiments. Thus, in 1998, Bruce O. Mansell and Edward D. Schroeder observed an average increase of 16 mg / l in the oxidizability of filtered water [8]. In 2000, Greenan et. al. observed an increase in water oxidizability in the range of 0-45 mg / l in the case of denitrification using heterotrophic bacteria [9].

Also, to result in quality effluent, treatment plants using biofiltration in Europe and the United States have included post-treatment steps to remove compounds resulting from filtration [10].

The main disadvantages observed are:

- The amount of organic matter present in the effluent of the filtration stage is high, which can affect the quality of the treated water, being necessary for an additional treatment stage to eliminate the resulting organic compounds;
- The priming time of the process is very long (1-2 months), much longer compared to the priming time of the other processes currently used for water treatment with high concentrations of nitrates;
- Because the start time of the process is very long, it is necessary to carefully maintain and monitor the biomass to prevent its loss and consequently to stop the process until the generation of new biomass.

The main advantages of using biological denitrification processes observed in experimental tests are:

- The process does not result in residue as in the case of reverse osmosis or ion exchange technologies;
- The process is effective in reducing the amount of nitrates regardless of the amount of nitrates influence;
- The highest amount of nitrates was reduced in the first part of each filter so that in the first 30 cm of the filter layer the influential amount of nitrate was reduced by 90%. As a result, in biological filtration, the active height of the filter represents approximately 30% of the total height of the filter.

Determining the right treatment technology is not an easy task due to many factors that need to be considered such as the amount of water to be treated, the characteristics of the raw water, the characteristics to be obtained for the treated water, etc.

To determine the most advantageous treatment scheme, it is necessary to carry out studies and tests for each type of technology to determine the quality of the resulting water for each technology, the need for pre- and / or post-treatment steps, and the treatment limits of each technology. , storage and treatment of waste obtained after treatment and an estimate of the costs involved in each technology.

From the variety of technologies available for reducing the amount of nitrates in water, biological denitrification is an efficient solution that can treat waters with large amounts of nitrates, can take large variations of loading, and can prove to be a cheaper and easier to implement solution than commonly used solutions such as ion exchange technologies and reverse osmosis.

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ANNEXES

APPENDIX - DISTRIBUTION OF REDUCTION OF NITROGEN CONCENTRATION INSIDE BIOFILTERS

Experimental cycle 1

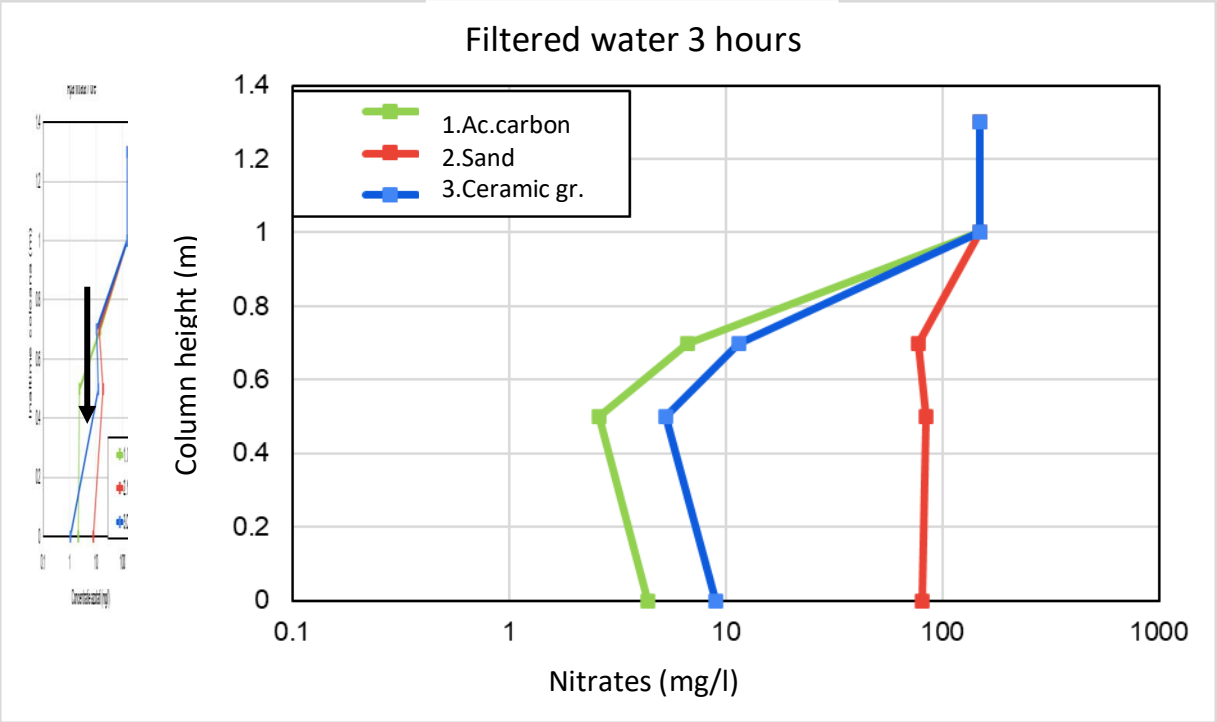

Figura.A-1. Distribution of the reduction of the nitrogen concentration in the filter layer - 3 h

Experimental cycle 2

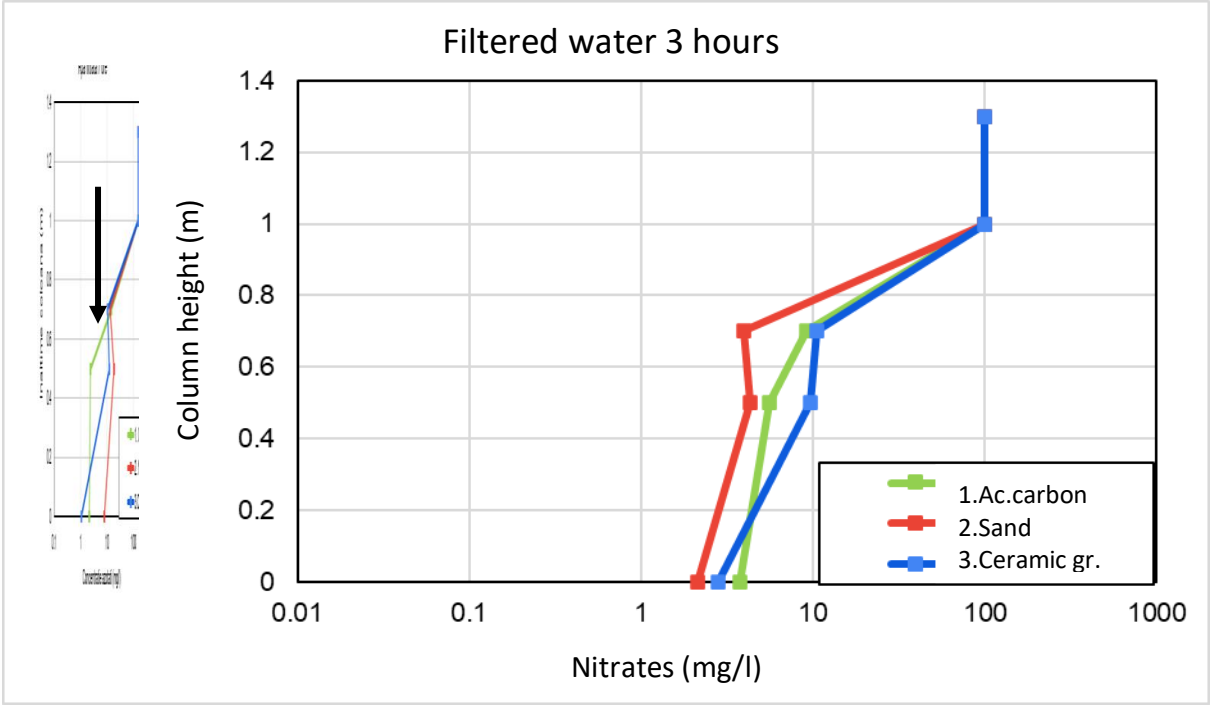

Figure A-2. Distribution of the reduction of the nitrogen concentration in the filter layer - 3 h.

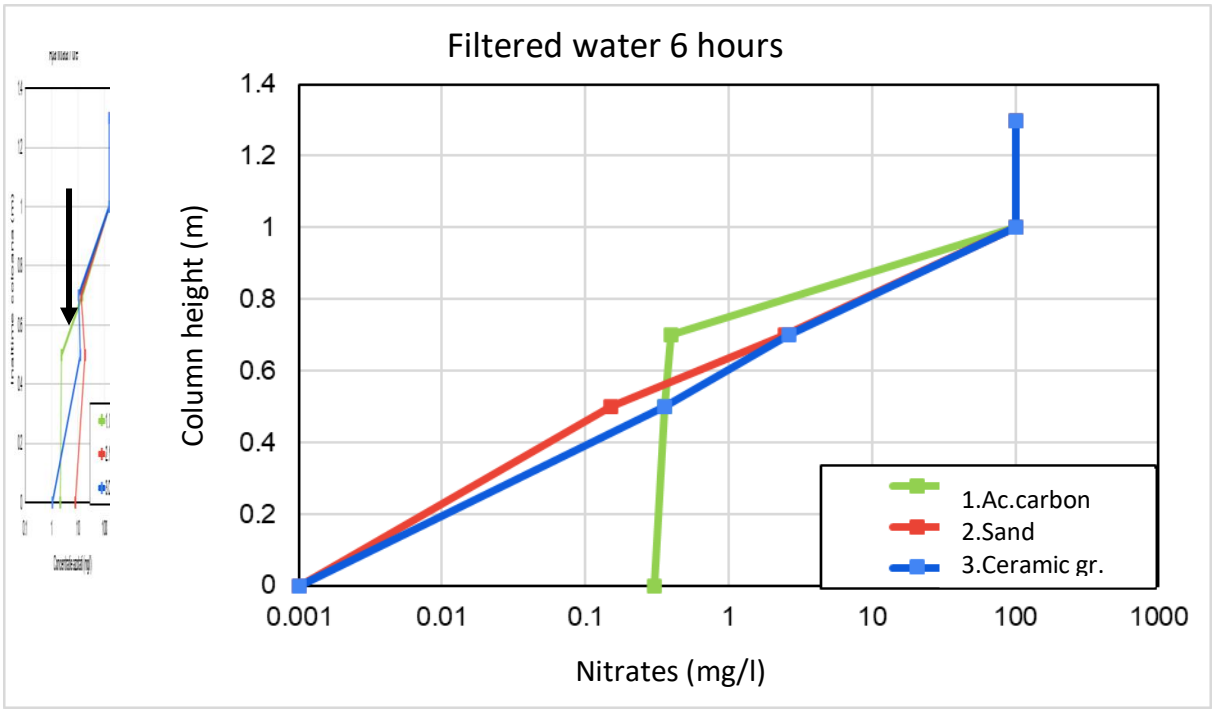

Figure A-3. Distribution of the reduction of the nitrogen concentration in the filter layer - 6 h.

Experimental cycle 3

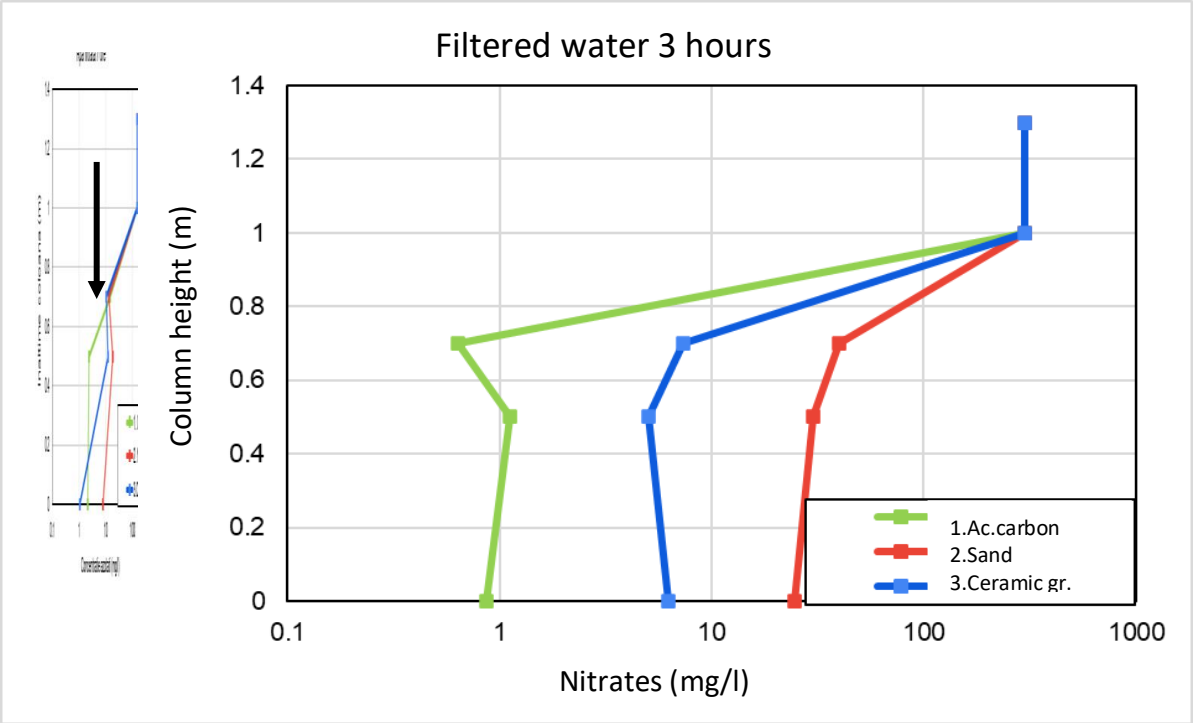

Figure A- 4. Distribution of the reduction of the nitrogen concentration in the filter layer - 3 h.

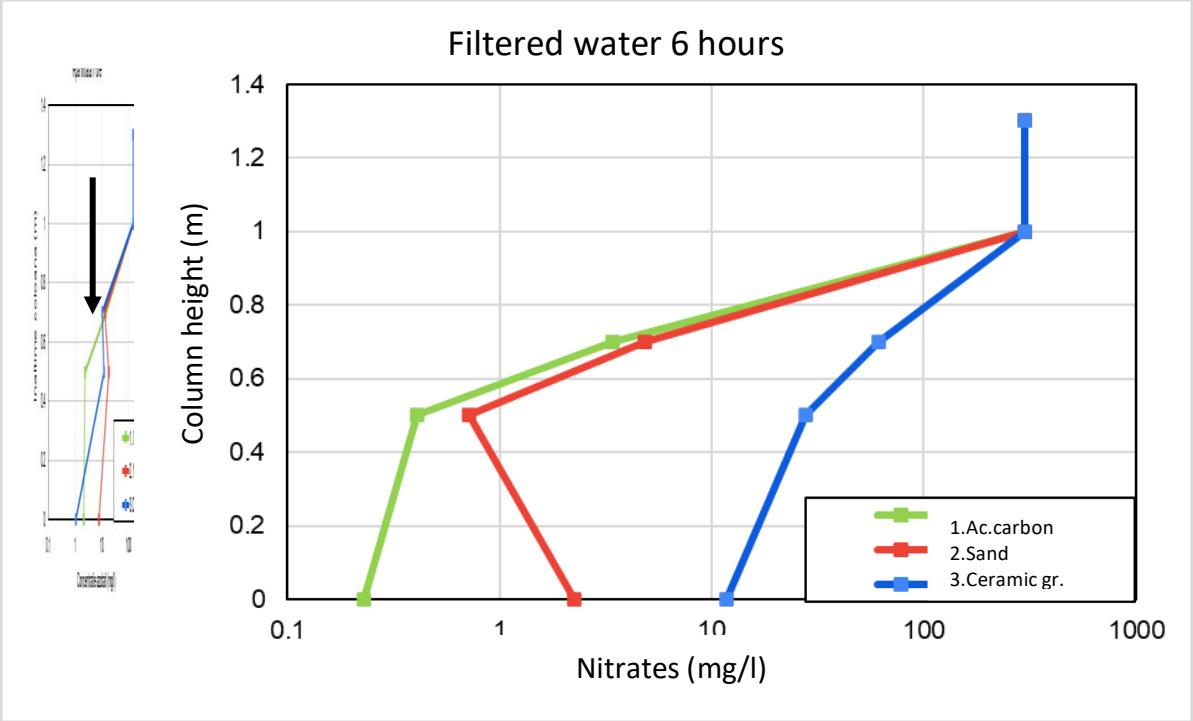

Figure A-5. Distribution of the reduction of the nitrogen concentration in the filter layer – 6 h.

APPENDIX 2 – VARIATIA OXIDABILITATII APEI

Experimental cycle 1

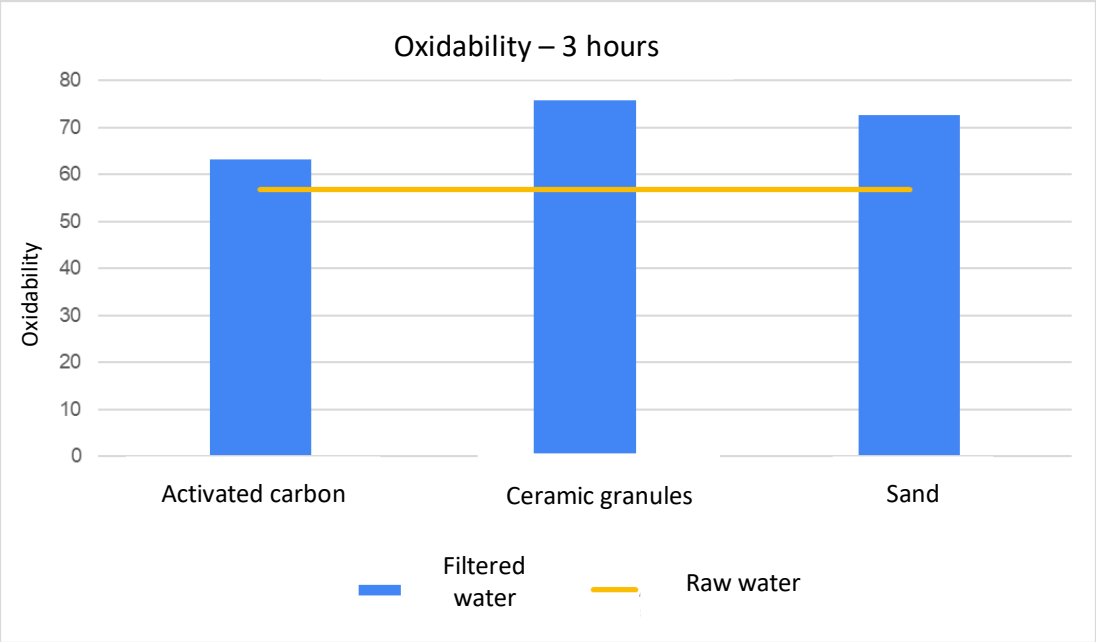

Figure A-6. Oxidability - filtered water - 3 h.

Experimental cycle 2

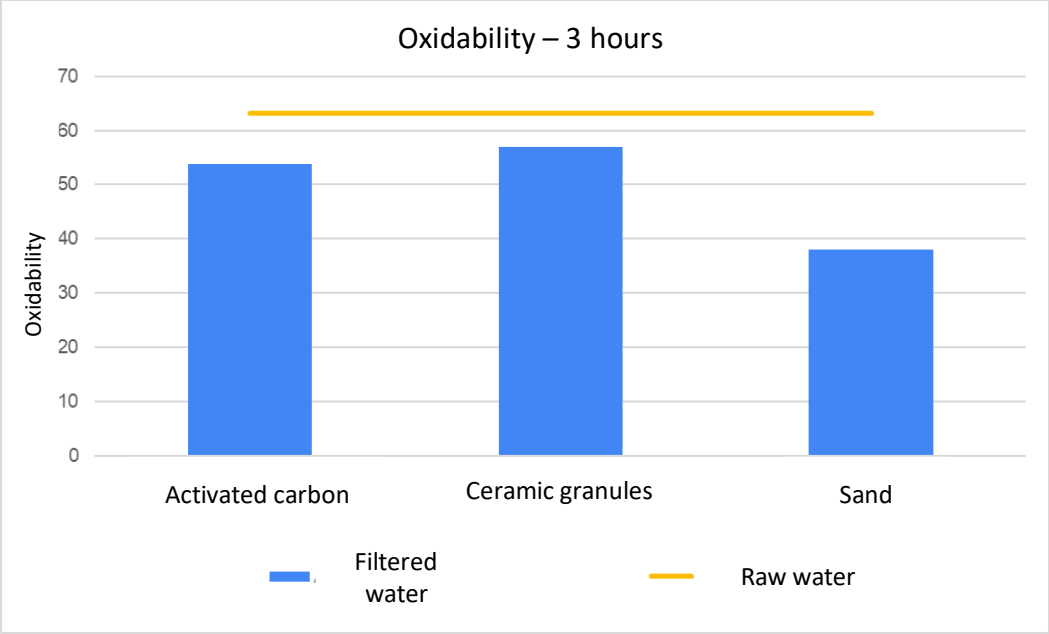

Figure A-7. Oxidability - filtered water - 3 h.

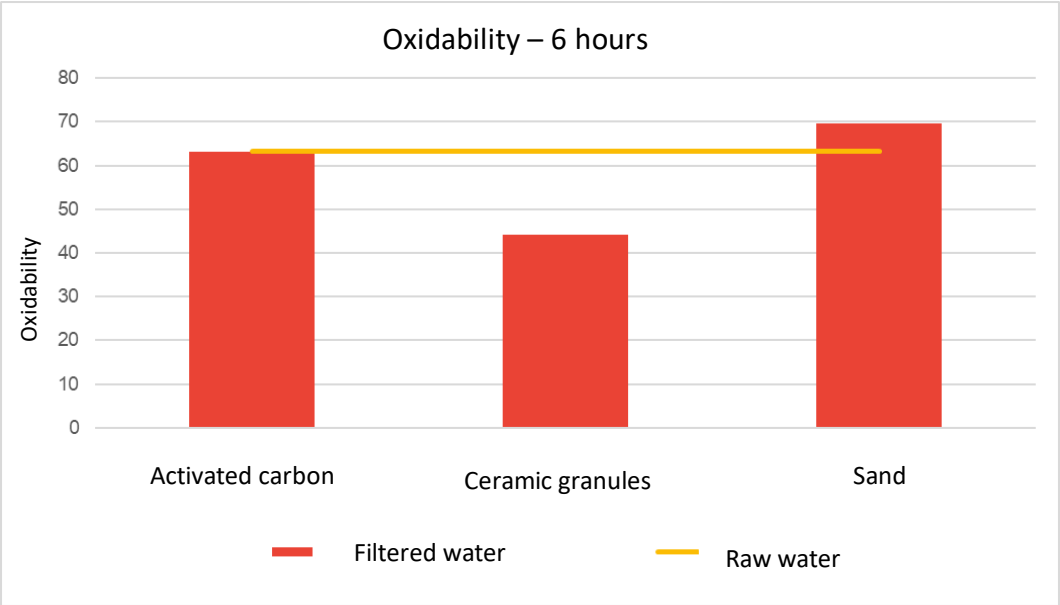

Figure A-8. Oxidability - filtered water - 6 h.

Experimental cycle 3

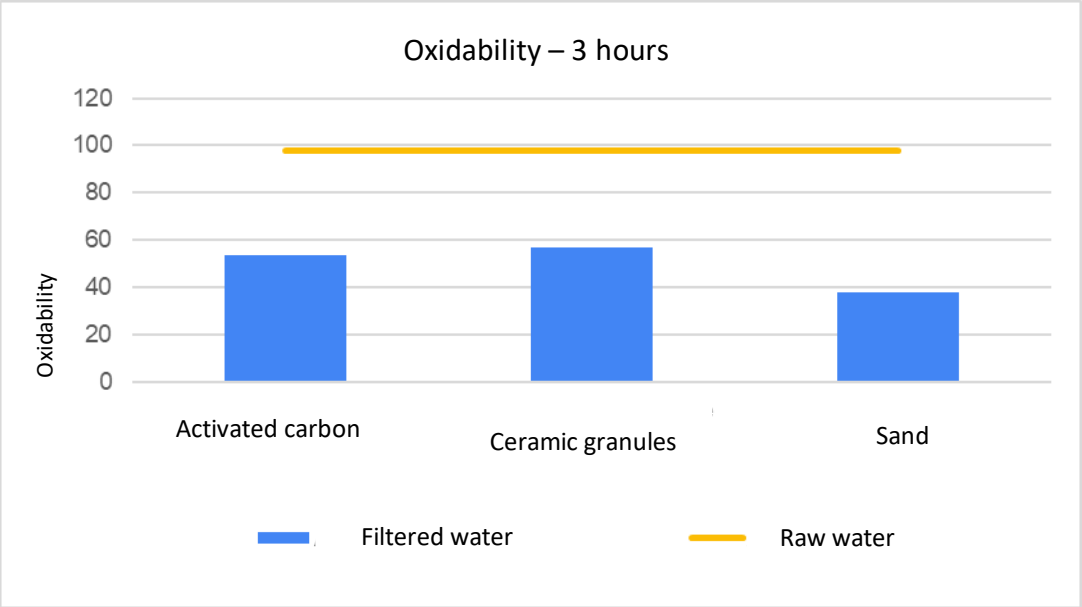

Figure A-9. Oxidability - filtered water - 3 h.

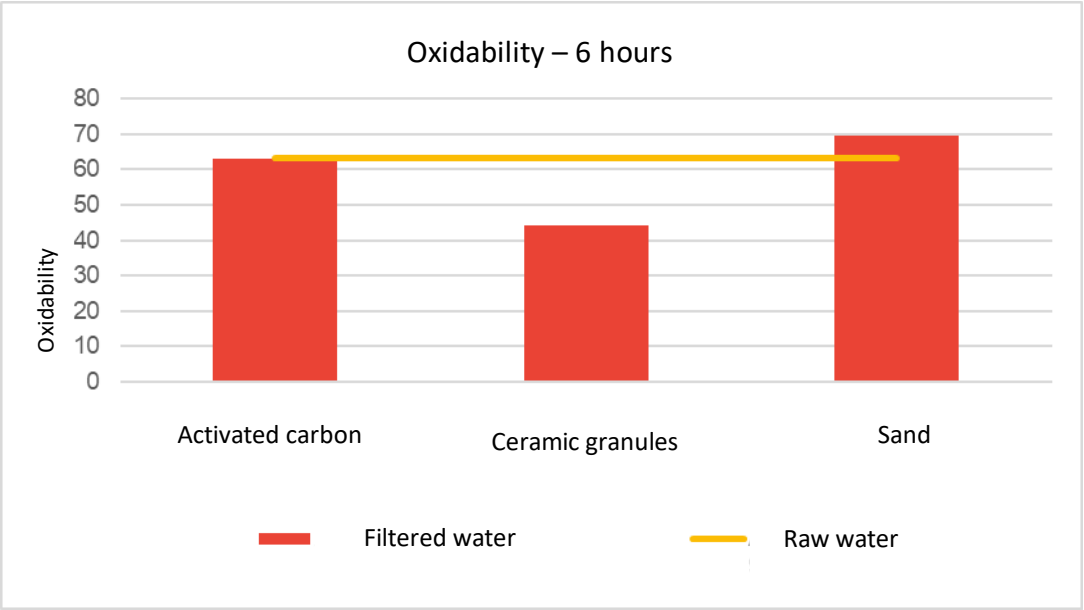

Figure A-10. Oxidability - filtered water - 6 h.