UNIVERSITATEA **POLITEHNICA** DIN BUCUREŞTI
Facultatea de Chimie Aplicată și Știința Materialelor

TRATAREA BIOLOGICĂ A APELOR DIN SURSE SUBTERANE IN VEDEREA POTABILIZĂRII

BIOLOGICAL TREATMENT OF GROUNDWATER INTENDED TO HUMAN CONSUMPTION

THESIS SUMMARY

Scientific Coordinator:
Prof. Emer. PhD. Eng. Gheorghița JINESCU

PhD. Student:
Eng. Ion-Viorel Pătroescu

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SUMMARY

INTRODUCTION

Water is an essential element of human life, its main domestic uses being drinking, preparing food and maintaining personal hygiene. Providing enough water for all community members in safe sanitary conditions must be a permanent concern of local communities and central authorities. The sanitary safety concept involves providing acceptable health risk of disease by using water from the development and implementation of risk management strategies from source to consumer. The purpose of risk management strategies identify risks, and ways of minimizing them are aimed at containing the dangerous constituents in the water and typically include a nationally / regionally legislative framework developed scientifically, but that also takes into account local environmental, economic and sociocultural conditions, a capable management system (proper infrastructure, accurate monitoring, efficient management) and an independent supervision and control system.

Water supplied to the human consumer, characterized by the attribute “potable”, must be safe for human health microbiologically, chemically and radiological, and must have approved organoleptic properties (no taste, odor and color).

Ensuring sanitary safety of drinking water from a microbiological point of view is achieved through disinfection, the destruction of pathogenic microorganisms, essential in any potability stream. The disinfectant agent widely used is chlorine. The use of chlorine as a disinfection agent aims both at destroying pathogens from the water – a result of fecal contamination of the sources and also, at preventing contamination (residual disinfection) of distribution networks to consumers. Since chlorine is less effective against certain pathogens, the management strategy should provide for a system of successive barriers against them (source protection, appropriate treatment stream including removal of the suspension before disinfection, protection of the treated water deposit and of the distribution system).

There are many constituents of raw water that can lead to health problems through long-term consumption, and a few that can have acute toxic action.

Also, the use of chemical reagents for disinfection, particularly of chlorine, in connection with certain chemical compositions of the raw water can lead to the formation of secondary disinfection products that can, at their turn, cause health problems and can give water unacceptable organoleptic properties.

To ensure the safety of water chemically, it is necessary to apply a treatment/potability flow adapted to the chemical composition of the raw water source, capable of reducing the concentrations of chemical constituents under the limits set by the regulations in force.

Treatment flows are chains of technological operations, of physical, chemical or biological nature, that must ensure the quality of the drinking water according to the applicable legislative framework, with the treatment cost managed by the consumer. There are technological and financial reasons that determine the choice of a certain operation in favor of another, and its position in the treatment system. A good example in this respect is represented by the potabilization of water sources with high ammonia concentrations.

The chlorine disinfection of these raw waters, the simplest treatment stream, cannot be applied singularly because the chlorine reacts with the ammonium and no longer achieves its disinfection and residual flux density. The potability stream must be completed with at least one operation of ammonium removal, chemical or biological, prior to the disinfection. Based on technological reasons (high dosage of chlorine, reactant agents over the admitted levels, organoleptic problems) and financial reasons (high operating costs), the correct operation is to remove the ammonium biologically (nitrification).

In Romania, there are many cases of inadequate potabilization of groundwater sources with high levels of ammonium, by using treatment systems that do not contain a stage for ammonium removal, prior to the chlorine disinfection.

Internationally, although biological nitrification has been studied for a long time, the results available in the relevant published literature are difficult to apply in real situations. This paper aims to determine the reaction conditions for the biological removal of ammonium from raw groundwater sources and to promote the implementation of these operations in the operational or projected treatment streams, where appropriate in Romania.

Key words: groundwater, drinking water, ammonium-nitrogen, nitrification, aerated biological filter, filter media, expanded clay, ammonium removal rate

PART I: CURRENT STAGE OF RESEARCH REGARDING THE BIOLOGICAL TREATMENT OF GROUNDWATERS

CHAPTER 1: NITROGEN IN THE ENVIRONMENT

This chapter presents relevant data and information concerning the presence of nitrogen in the environment – compounds of nitrogen, transformation and transportation mechanisms involved in the nitrogen cycle, effects of nitrogen discharge into the environment.

Nitrogen is present in the environment, in seven oxidation states (-3, 0, +1, +2, +3, +4, +5), and its important chemical compounds for water treatment/ purification are: N-organic, NH_3/NH_4^+, N_2, NO_2^-, NO_3^- .

The main transformation and transportation mechanisms performing the nitrogen cycle in nature are: fixation, ammonation, synthesis, nitrification and denitrification.

The natural cycle of nitrogen was disrupted by the 10% increase of the amount of fixed nitrogen gas, from the beginning of agriculture until now, which is found solubilized in the hydrosphere, its cause being human activities such as: cultivation / soil fertilization, animal growth and poor management of animal and human waste water.

It describes the negative effects of nitrogen discharges on the environment (eutrophication, depletion of oxygen concentration dissolved in surface waters, aquatic toxicity) and on human health (methemoglobinemia, carcinogenicity and potentially, birth defects).

CHAPTER 2: THE NECESSITY OF POTABILITY. QUALITY PARAMETERS OF DRINKING WATER

This chapter deals with the information that substantiates the necessity of potabilization, water sources destined for human consumption, parameters and values regulated for drinking water, as well as the methods monitoring the quality of the drinking water.

Thus, it shows the implications of the presence in the drinking water of a certain number of contaminants of interest for the subject of this thesis - ammonium, nitrite, nitrate, chlorine, trihalomethanes, chloramines, manganese, iron - on consumers' health and the safe concentrations for long term consumption, determined through clinical trials, or the reasons why it is / is not necessary to limit the concentration of certain values.

It presents the quality regulations regarding drinking water in Romania, which are, as expected, almost identical to those in the European Union, and the flow of treatment depending on the composition of raw water.

It also describes standard methods for determining the values of some quality physical-chemical parameters (pH, rH, dissolved oxygen, free/ total chlorine, turbidity, alkalinity, hardness, cation / anion mix, ammonium, manganese, iron, total / dissolved organic carbon, THMs) and biological parameters (Escherichia coli and coliform bacteria, intestinal enterococci, Clostridium perfringens, cultures of micro-organisms, Pseudomonas aeruginosa) of water, directly connected to, or related with the topic of this thesis.

CHAPTER 3: BIOLOGICAL TREATMENT PROCESSES

This chapter presents:

- the main classes of micro-organisms found in waters (eukaryiotes, bacteria, viruses, archaea) and their properties;
- structure, composition, metabolism and breathing of bacterian cells, as well as the speed of bacterian processes;
- methods of ammonium removal from water - physical, chemical (complete oxidation of molecular nitrogen with chlorine) and biological (nitrification);
- properties of nitrification bacteria and the limiting nitrification factors;
- nitrification processes of raw waters, in view of to making it potable, and of waste waters for treatment - activated sludge with biomass attached on inert carrier (on fixed layer, on mobile layer), hybrid processes, intensive methods of contacting phases;
- aspects of mathematic defining - mathematical modeling - empirical models and regression analysis, developing the shape of the model and processing of experimental data, as well as the correlation analysis, and also, the procedures mentioned in the literature on programming experiments (monofactorial experiment, factorial experiment, Box-Wilson experiment type).

From the critical study of the presented information, it is considered appropriate for the nitrification of raw groundwater for drinking purposes, to use the biofiltration process with upward movement of the influent (the nitrification rates in the 0.25 to 0.60 kg N/m^3/day), and for the mathematical modeling and processing of the empirical models of polynomial type, regression through the method of the smallest squares and correlation analysis.

PART II: EXPERIMENTAL RESEARCH REGARDING BIOLOGICAL TREATMENT OF WATERS FROM UNDERGROUND SOURCES

In the context of the presence of ammonium ions in the raw water intended for human consumption, of the effects that this presence induces on the disinfection and of the necessity to adapt the treatment flow of the existing drinking water treatment plants to this unwanted reality, this paper has the following objectives:

- analytic characterization of raw groundwaters meant for treatment process, focusing on parameters that are directly related to, or connected to the ammonium ions;
- highlighting the non-compliace of the raw groundwater quality to the applicable regulations;
- establishing the treatment flows, capable of ensuring the proper quality of the drinking water in relation to the faulty parameters;
- determining the optimum value of the technological parameters for the operations through which the faulty parameters become compliant to the optimum values;

- identifying the recommended methods of the ammonium ions removal until it reaches the the regulated value admitted in the drinking water, according to its concentration in the raw water;
- highlighting the cases where it is necessary to introduce it in the treatment flow of the nitrification process;
- conceving and implementing of a pilot lab installation with continuous operation for biological removing of the ammonium ions from the raw groundwater;
- selecting the type of inert media filter suitable for nitrification;
- characterization of the media filter and demonstrating its inert nature;
- identifying optimal granulation for the inert media filter;
- determining the nitrification performance depending on the raw water quality parameters and its operating parameters;
- revealing the concentration range of the anorganic compounds of nitrogen in the nitrification biofilter;
- determining the dependence relation between the nitrification speed and the temperature of the raw water by modeling the process and mathematical processing of the experimental data;
- determining the dependence relation between the required height of the filter media bed for complete nitrification of ammonia present in the raw water and raw water parameters, by the nitrification process modeling and mathematical processing of experimental data;
- technological sizing of the nitrification biofilter, based on raw water parameters and operating parameters.

CHAPTER 4: PHYSICAL-CHEMICAL CHARACTERISTICS OF GROUNDWATERS

This chapter presents the standardized methods of characterizing raw groundwaters and also, the analytical equipment required.

Also, it shows the characterisation data/values of physical-chemical parameters (pH, NH_4^+, NO_3^-, NO_2^-, PO_4^{3-}, Fe, Mn, alkalinity, total/dissolved organic carbon, turbidity, hardness) for a few groundwater sources from Romania, used for the process of drinking water: S1-S6/Ilfov, S7-S8/Călăraşi, S9/Vrancea and S10-S11/Gorj. Sites were selected based on the need to adapt existing treatment flows to source composition.

The analysis of the chemical composition of raw groundwaters revealed that the main noncompliances of maximum alloweble concentrations (MACs) were registered at the following quality parameters:

- ammonium (concentrations higher than MAC = 0.5 mg/L) at all sources:

-S1: 3 – 7.4 mg NH_4^+/L;
-S2: 1.9 – 6.5 mg NH_4^+/L;
-S3: 1.3 – 2.2 mg NH_4^+/L;
-S4: 1.2 – 2.2 mg NH_4^+/L;
-S5: 0.6 – 1.01 mg NH_4^+/L;
-S7: 0.66 – 1.5 mg NH_4^+/L;
-S8: 0.19 – 4.04 mg NH_4^+/L;
-S9: 0.53 – 0.75 mg NH_4^+/L;
-S10: 0.65 - 7 mg NH_4^+/L;
-S11: 3.63 – 4.38 mg NH_4^+/L;

- iron (concentrations higher than MAC = 200 µg/L) – at most sources:

-S3: 390 – 780 mg/L;

-S4: 600 - 650 mg/L;
-S5: 140 - 410 mg/L;
-S7: 120 - 2400 mg/L;
-S8: 24 - 930 mg/L;
-S9: 522 - 950 mg/L;
-S10: 520 – 8400 mg/L;
-S11: 60 - 1600 mg/L;

- manganese (concentrations higher than MAC = 50 µg/L) – at most sources:

-S3: 130 - 150 mg/L;
-S4: 150 - 200 mg/L;
-S5: 98 – 161mg/L;
-S6: 146 – 180 mg/L;
-S7: 68 – 132 mg/L;
-S8: 5 – 230 mg/L;
-S9: 145 - 160 mg/L;
-S10: 10 – 110 mg/L;

- hardness (lower than MAC = 5 German degrees) – at the sources:

-S1: 2.5 – 3.4 German degrees of hardness;
-S2: 2.8 – 6.5 German degrees of hardness.

The results of analyses on raw groundwater sources from S1-S11 sites indicates the need for systematic research in order to set up complex physical – chemical and biological treatment flows, with an emphasize on sizing issues.

CHAPTER 5: EXPERIMENTAL RESEARCH TO DETERMINE THE TREATMENT FLOWS

The quality characterisitics of certain raw groundwaters used for the preparation of drinking water determins the complexity of treatment flows and the parameters of the technological processes to correct the non-compliances.

Starting from the values of the quality parameters determined at the characterization of raw groundwater, in view of correcting the identified non-compliaces, it is necessary to make experimental lab researches for each location, in order to prove that certain recommended technological treatment processes comply to MACs and thus, determining the values of the operating parameters (reagent doses, reaction time, filtration rate).

Three study cases are presented to sustain this theory, referring to sources S1 and S2, S5 and S6/Ilfov and S9/Vrancea.

5.1 CASE STUDY 1 – SOURCES S1 AND S2, ILFOV COUNTY

Characterization of underground raw waters from these locations have shown similar compositions, so that the necessary treatment flows should be just as similar, which is why the two locations represent one case. The analysis of the values of quality parameters from the sources and their comparison with the MAC, reveales the non-compliances:
-concentration of NH_4^+ > MAC = 0.5 mg/L (S1: 3-7.4 mg/L; S2: 1.9-6.5mg/L);
-hardness < min. 5 German degrees of hardness.

Other parameters, with possible implications on the treatment flow (Fe, Mn) have lower values than the MACs.

The indicator of the total organic carbon has values that must be tested in relation to the possibility of forming undesired by-products from the chlorination treatment.

To establish the technological treatment process, starting from the quality nonconformities, treatability tests were performed on momentary samples of influents of the treatment plants (mixed wells of raw groundwater) in locations S1 and S2, as follows:
- evaluation potential of forming trihalomethanes (THM) and chloramines from chemical oxidation of ammonium by chlorination method to breakpoint;
- correction of the hardness at a value of minimum 5 German degrees of hardness.

Due to the great mass ratios (Cl_2 : NH_4^+- N = 8 : 1**)** necessary for the chemical oxidation of ammonium and to the high concentrations of NH_4^+ from the raw groundwater, high doses of chlorine must be used (considering that the ammonium concentrations used at testing - 2.37 mg NH_4^+/L for S1 and respectively 1.48 mg NH_4^+/L for S2 – have been very different from the highest concentrations found in the raw groundwater from the two locations, the dose of chlorine has reached values of 11.84 to 19.85 mg Cl_2/L). These unusual chlorine doses, in combination with the reactive loading of dissolved organic carbon (DOC) from the raw water - 3.3 mg C/L for S1 and, respectively, 3.1 mg C/L for S2 - lead to higher values of concentration of THMs than the regulated limit - 100 µg/L, right from the treatment day (148 µg/l for S1 and 114 µg/l for S2). Among the species of THMs, trichloromethane (TCM) is majoritary (> 92%) 6 days from the reaction, under the conditions of a concentration of bromide in the tested raw waters <100 µg / L)

Except for the formation of the trichloromethanes, at the chlorine oxidation of ammonium, there are others undesired side effects, and in order to highlight them, analytical testing has been performed:

- chloramine formation that can induce taste and smell to the drinking water – the level of free residual chlorine is lower than the minimal value imposed by 80% of the total residual chlorine;
- the pH of the treated water decreases below the minimal value of 6.5, so that it is necessary to correct it;
- the mass ratio Cl_2 : NH_4^+-N = 8.2 :1 is not high enough to take the NH_4^+ concentration below MAC = 0.5 mg/L; according to the properties of the raw water, this ratio can go up to 15:1.

Considering the necessary high doses of chlorine, with negative influences on the potabilization cost, and of the emergence of secondary reaction agents (THMs, chloramines), in concentrations higher than the maximum admitted values, the oxidation of the ammonium nitrogen (NH_4^+-N) through chlorination at the breakpoint does not represent an option for sources S1 and S2/Ilfov, so that nitrification becomes the only option to consider.

The actual solution proposed for the correction of hardness in the case of underground water from S1, which constantly presents values of the total hardness below the mimimum admitted concentration (min. 5 german degrees), is treating it with solutions of calcium chloride and sodium bicarbonate:

$$CaCl_2 + 2NaHCO_3 \rightarrow Ca^{2+} + 2HCO_3^- + 2NaCl \quad (79)$$

For the two sources that make one case study, S1 and S2, the potability flow chart considered necessary, consists of the processes and parameters from Figure 31:

- biological nitrification for the NH_4^+ oxidation to NO_3^-, for the operating parameters that must be determined experimentally;
- rapid sand filtration (w_f = 10 m/h), to retain the biomass in suspension;
- granular activated carbon (GAC) filtration (t = 5 min.), for the decrease of THMs predecessors (removal rate of TOC < 30%);
- hardness adjustment;
- chlorine disinfection (t = 30 min.), for network remanence.

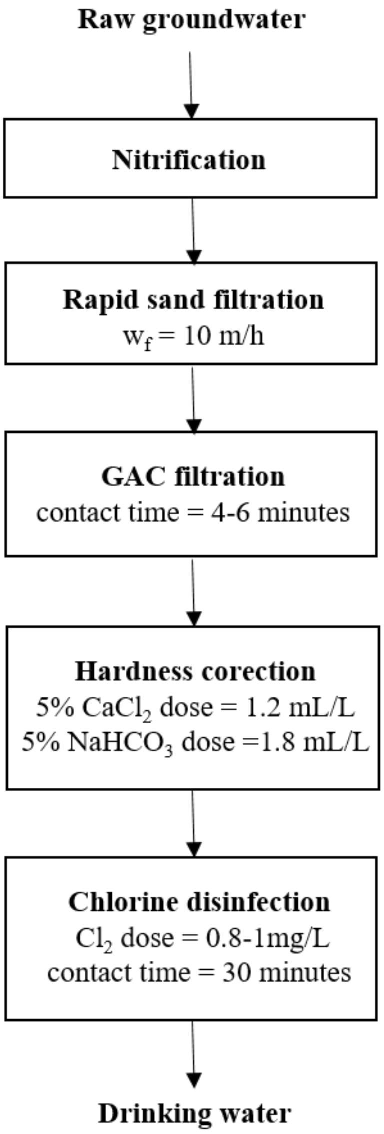

Figure 31. Potability flow recommended for sources S1 and S2/Ilfov

5.2 CASE STUDY 2 – SOURCES S5 AND S6, ILFOV COUNTY

Just as in the previous case study, the similar composition of raw groundwaters, determined to consider the two locations as one single case study, and the main identified non-compliances of regulated values of quality indicators are:

- concentration of NH_4^+ > MAC = 0.5 mg/L (S5: 0.6-1.01 mg/L; S6: 0.4-1.34 mg/L);
- concentration of Mn > MAC = 50 µg/L;
- concentration of Fe > MAC = 200 µg/L.

In order to determine the technological process of potability, starting from non-compliances in the quality of raw groundwater, treatability tests were conducted on momentary samples of inffluents in the treatment plants (mixed wells of raw groundwater) in sources S5 and S6:

- Mn oxidation (II) and Fe(II) with chlorine and precipitation oxides / oxyhydroxides;
- filtration on manganised sand;
- oxidation NH_4^+ through chlorination at the breakpoint.

For the two sources, S5 and S6, the potability flow chart considered necessary includes the operations and parameters from Figure 32:

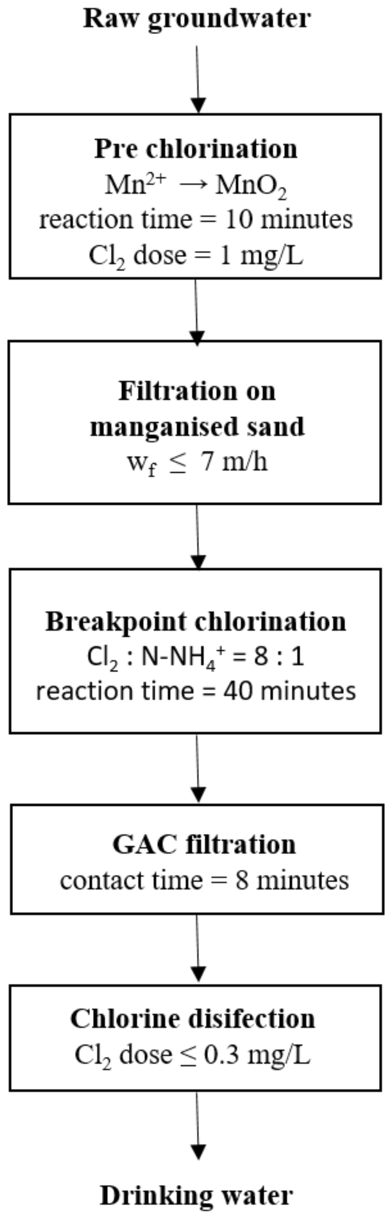

Figure 32. Potability flow recommended for sources S5 and S6/Ilfov

5.3 CASE STUDY 3 – SOURCE S9, VRANCEA COUNTY

The main identified excedances of standardized values of quality indicators are:

- concentration of NH_4^+ > MAC = 0.5 mg/L (0.53-0.75 mg/L);
- concentration of Fe (soluble/ionic) > MAC = 200 µg/L (47-370 µg/L).
- concentration of Mn (soluble/ionic) > MAC = 50 µg/L (130-141 µg/L).

Based on these non-compliances, to establish the technological process of potability,it was considered necessary to conduct these treatability tests on a momentary sample from S9 (pH = 7.58, Fe^{2+} =370 µg/L, Mn^{2+} = 130 µg/L):

- oxidation of NH_4^+ through chlorination at the breakpoint and evaluating the potential of trihalomethane (THMs) and chloramine formation at the chemical oxidation of ammonium through the breakpoint chlorination method;
- establishing the optimum variant for metal ions removal (Fe_s, Mn_s) through oxidation/ precipitation (nature and dose of oxidant, reaction parameters);

From the $NH4^+$ oxidation experiment by chlorination at the breakpoint under the reaction conditions - Cl_2:N-NH_4^+ = 8.2:1, reaction time = 30 min., with the following results: remanent NH_4^+ < 0.1 mg/L, free residual Cl_2/ total residual Cl_2 = 0.70, THMs = 2.9 µg/L.

Iron oxidation is done by aeration and for the oxidation of manganese, three oxidizing agents were tested – Cl_2, NaOCl, KMnO4 – under the conditions: doses of oxidants: Cl_2 = 1 - 1.5 mg/L, NaOCl = 1-2.1 mg/L, $KMnO_4$ = 0.3 mg/L; reaction time: 10-30 min.; pH range: 7.5-9.5 at the oxidation with Cl_2 and NaOCl (correction with Na_2CO_3), 7.58 to oxidation with $KMnO_4$. The conclusion of the series oxidation experiments of Mn^{2+} is that the optimal solution for oxidation is the one with $KMnO_4$, because bringing Mn^{2+} under CMA (50 µg/L) occurs at the pH of the raw water within a short reaction time (10 min.) and at a dose close to the stoichiometric one (0.3 mg/L).

For source S9, the potability flow chart to be applied, includes the following operations and reaction parameters from Figure 33:

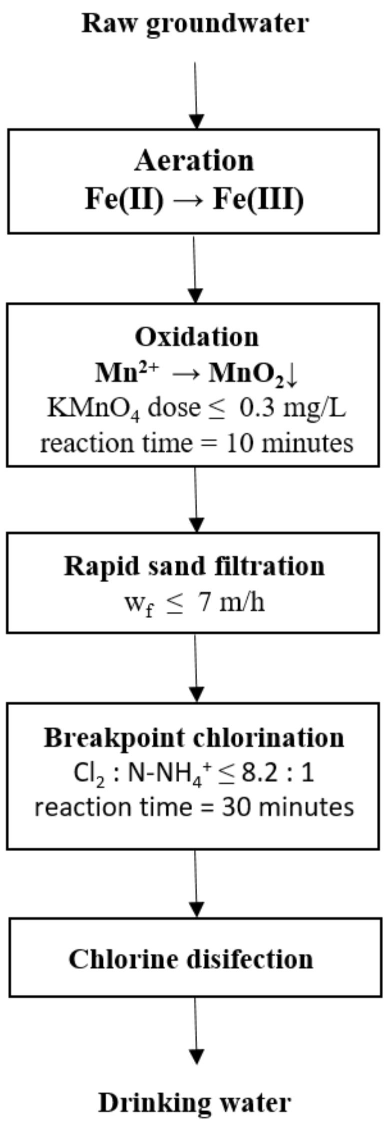

Figure 33. Potability flow recommended for source S9/Vrancea

From the case studies previously described, there is a series of conclusions regarding the implications of the presence of ammonium in the raw water intended for human consumption:

- the ammonium must be removed before the disinfection process, because it compromises it by reacting with the chlorine destined for it;
- in theory, the ammonium removal from water can be achieved chemically, through chlorination at the breakpoint, chlorine being the only reagent capable to perform a complete oxidation of the ammonium;
- chlorination at the breakpoint requires high mass ratios Cl_2 : $N\text{-}NH_4^+$ (minimum 8:1) which means high reagent consumption, with the afferent costs;
- the ammonium oxidation with chlorine implies introducing chloride ions in the drinking water;
- when there are high concentrations of ammonium, through chlorination takes place the decrease of the pH, which require correction, meaning using other reagents, with the associated costs, and the introduction of ionic species in the drinking water;
- through the oxidation of ammonium with chlorine result secondary by-products, trihalomethanes and chloramines, and they are also regulated because of their harmfulness;
- the quantity of secondary products depends on several factors, including the dose of chlorine used, determined in its turn by the ammonium concentration in the raw water;
- removal of chloramine and partially, of trihalomethanes, can be achieved by adsorption on granular activated carbon.

The general conclusion that can be drawn from the three case studies is that the chemical removal of ammonium is a process that poses problems and nitrification seems like a more appealing solution since it does not require chemical reagents, even if it's more difficult to implement in an existing technological flow and is more sensitive when the process is unfolding.

However, in specific cases where there is an existing treatment flow, for relatively low concentrations of ammonium ions in the raw water, the decision should be based on the best choice from an economical point of view, taking into account the local restrictions (configuration and flexibility of the existing station, the sustaining the cost, the existence of skilled labor force, ensuring electricity supply at stable parameters).

Based on water sources analyses, it is recommended to the supplying of drinking water at the regulated parameters of a community, to be solved considering the following options, in the order they are presented:

- as much as possible, to identify and use a free ammonium raw water source;
- if the first option is not possible, then one must find and use a raw water source with an ammonium concentration lower than 1.5 mg/L, for which chlorination at breakpoint can be a solution with reasonable costs, easy to apply and exploit;
- if the second option is not possible either, then the raw water source with ammonium concentration higher than 1.5 mg/L must be subjected to a treatment flow which necessarily includes the nitrification process for the biological removal of ammonium.

CHAPTER 6: CHARACTERIZATION OF BIOLOGICAL FILTER MEDIA

To conduct the nitrification experiments, it was intended to use and test bioreactors filled with some filter media, hypothetically corresponding to the properties of the nitrification bacteria (size and poor adhesion to surfaces): granular mineral media (expanded clay) and random plastic media.

In order to be used as an inert carrier for fixing the nitrifying bacteria carrying out the biochemical process of ammonium oxidation to nitrate, it is necessary to know the physical-chemical properties of expanded clay, important for the process, as well as the elemental chemical composition, the inert character, surface morphology, size and pore surface area, density and particle size distribution of the granular material, void fraction and the density of the bulk material. For this reason, this chapter presents the characterization methods of the granular carrier used to develop biofilms, that is:

- elemental analysis (XRF) which reveals the qualitative elemental composition of the carrier and the concentrations of the constituent elements;
- analysis of leachate (ICP-MS), verifying the relation to the biological process;
- specific surface (BET);
- morphological analysis of particle surface (SEM);
- specific particle physical and geometrical properties;
- physical and geometrical properties of the granular layer.

Based on the analysis of literature data, out of a wider commercial range, two granulometric fractions of expanded clay were separated, 2-5 mm şi 4-10 mm, for which these determinations were made.

The XRF analysis identified 18 elements that are part of the expanded clay grains, used as inert filler, on which the nitrification bacteria develops inside the biological nitrification bioreactor, out of which the main percentage is represented by: silicon - 183 g/kg, aluminum – 96.6 g/kg, iron - 56.6 g/kg, calcium – 23.2 g/kg, manganese – 10.5g/kg and potassium – 14.9 g/kg.

Analysis of the leachate obtained after a contact time of 3 hours with expanded clay, much more than the contact time in a nitrification biofilter which is of 10 min., revealed concentrations of Cr, Hg, As, Pb, Co, Al, Se, Mo, Ni, Mn, Cd, Sb, Cu, Zn, Fe elements, lower than the MAC regulated by Romanian Law 458/2002, updated, which proves the inert character of the carrier in relation to the process.

The specific surface area calculated by BET method using the adsorption data in the range of relative pressures ranging from 0.05 - 0.3, led to the value of 0.715 m^2/g, nitrogen adsorbtion-desorption isotherms are of type IV, the pore size distribution is multi-modal, and the presence of hysteresis on the adsorption - desorption isotherms and its area indicates the presence of a small fraction of mesopores (2-50 nm), the sample containing predominantly macropores (> 50 nm), results available for samples of both granulometric fractions - 2-5 mm and 4-10 mm.

SEM surface analysis of expanded clay grains revealed uneven surfaces with macropores, favourable to the development of the nitrifying biofilm (Figure 43).

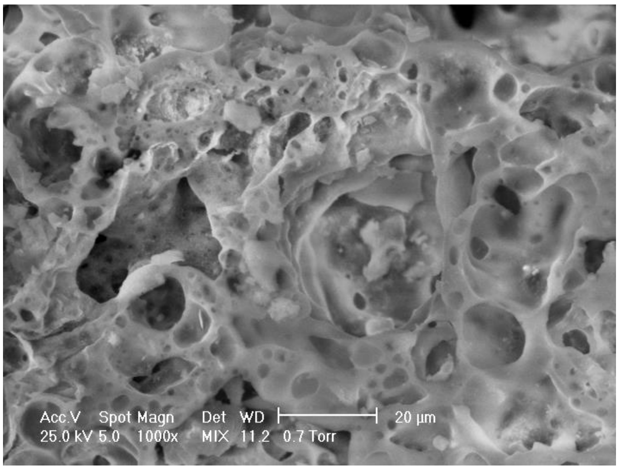

Figure 43. SEM picture of 1000x magnitude of the surface of a grain of expanded clay

Physical and geometrical properties of the granulometric fraction 2-5 mm (Figure 44) were determined experimentally (ε = 0.46; ρ_m = 820 kg/m^3; ρ_{bulk} = 440 kg/m^3; d10 = 2.3 mm and d50 = 3.1 mm - Figure 45) and of the granulometric fraction 4 -10 mm (ε = 0.50; ρ_{bulk} = 385 kg/m^3; d10 = 4.6 mm).

Figure 44. Expanded clay granulometric size 2-5 mm

Based on these experimental determinations, the two granulometric fractions - 2-5 mm and 4-10 mm – have been selected to be used in the nitrification experiments.

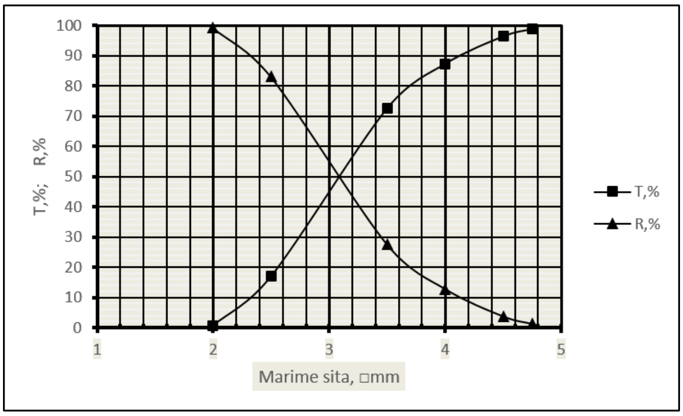

Figure 45. Graphical determination of significant diameters of the fraction 2-5 mm

A random plastic media type Kaldnes was also considered (ϕ x h = 16 x 9 mm, ρ_m = 750 kg/m^3, ρ_{bulk} = 250 kg/m, ε = 0.67, σ =750 m^2/m^3) for the nitrification experiments (Figure 47).

Figure 47. Random plastic media with nitrifying biofilm on the surface

CHAPTER 7: NITRIFICATION EXPERIMENTS

Performances of biofiltering systems for nitrification and not only, are strongly influenced by: environmental factors (temperature, dissolved oxygen, concentration of nutrients), parameters and process configuration (retention time, upward / downward movement, reverse backwash parameters) and properties of the environment used as filler.

The biological oxidation of ammonium can be achieved by using multiple types of bioreactors, but in order to make underground raw water potable, the most suitable would be the immersed filler bioreactors and, out of these, the aerated biofilters. Compared to other attached biomass systems, like the nitrifying trickling filters (NTFs), the biological aerated filters (BAFs) with granular material have significant advantages: high concentration of biomass, longer lasting biomass, high resistance to concentration shocks, dual functions - filtering and removal of pollutants, simple maintenance and operation, compactness. It must also be mentioned the few disadvantages: the risk of clogging and costs of the aeration and washing systems.

The conducted nitrification experiments had well targeted objectives:

- selecting the type of filler suitable to the nitrification process;
- identifying the optimal granulation for the inert filter media;
- determining the volumetric nitrification rates;
- modeling the dependence relation between the rate of the process and temperature;
- determining the concentration areas in the biofilter with granular carrier;
- defining the dependence relation between the height of the biofiltering layer necessary for the complete nitrification and the parameters of the influent and of the biofilter operation, so that it allows a pre-sizing of the nitrification biofilter.

Nitrification experiments have been performed in pilot lab instalations with continuous operation, designed and preliminary made, using a biofilm reactor with raw groundwater as influents, as such or with synthetically enhanced ammonium content.

7.1 NITRIFICATION EXPERIMENTS FOR THE SELECTION OF THE SUITABLE BIOFILTER MEDIA

The purpose of these preliminary experiments was to evaluate the comparative performance of the removal of ammonium-nitrogen for the two different types of media characterized in Chapter 6:

- Kaldnes type random plastic media made of cylindrical geometrical bodies with six rooms of plastic material and smooth surfaces;
- Granular mineral media of light expanded clay of granulometric size 4-6 mm.

The two types of media previously mentioned have equipped three aerated biological reactors at the pilot lab level, with continuous operation, operated in different hydrodynamical ways (Figures 49-51), at the following parameters:

- Kaldnes type media/upflow and aeration within the bed/ t=11-19.3°C, dissolved oxygen= 6.3-7.9 mgO_2/L, empty bed contact time (EBCT) =29-79 min., apparent filtration rate (w_f) = 1.27-3.44 m/h;
- Kaldnes type media/upflow of the influent and pre-aeration of the influent and effluent recirculation/ t=11.6-18.8°C, dissolved oxygen= 2.9-5.7 mgO_2/L, empty bed contact time =13-72 min., filtration rate =1.43-2.82 m/h;
- Light expanded clay aggregates (Leca) media/downflow of the influent and aeration within the bed/ t=15.4-18°C, dissolved oxygen= 2.5-6.7 mgO_2/L, empty bed contact time = 4-20 min., filtration rate =1.37-6.36 m/h.

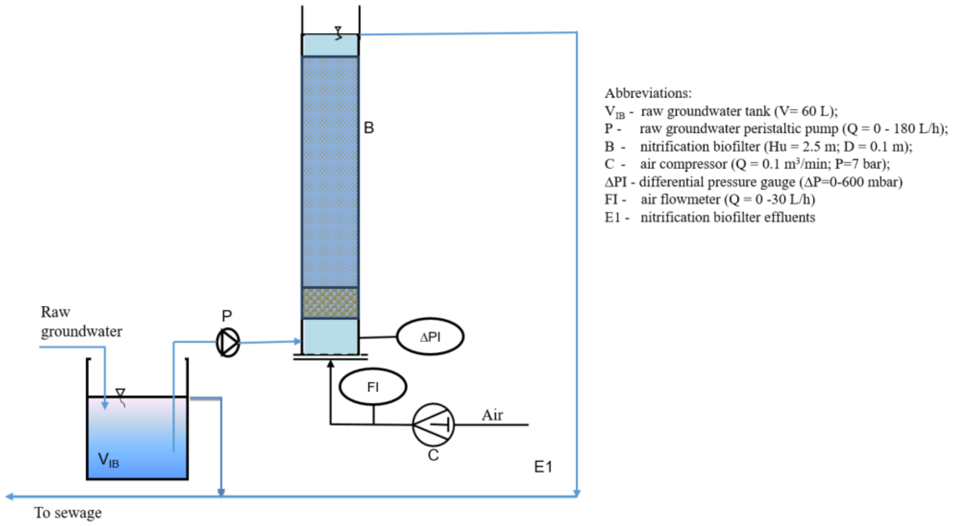

Figure 49. Pilot nitrification installation using an upflow bioreactor filled with Kaldnes media

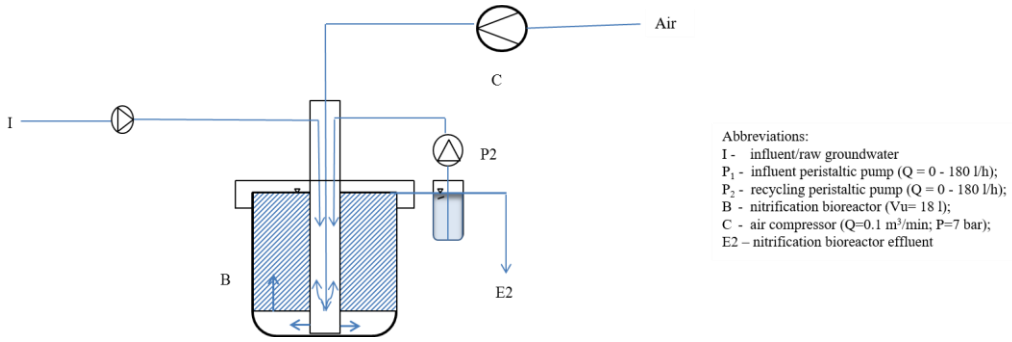

Figure 50. Pilot nitrification installation using a Kaldnes media bioreactor, with pre-aeration of the influent and effluent recirculation

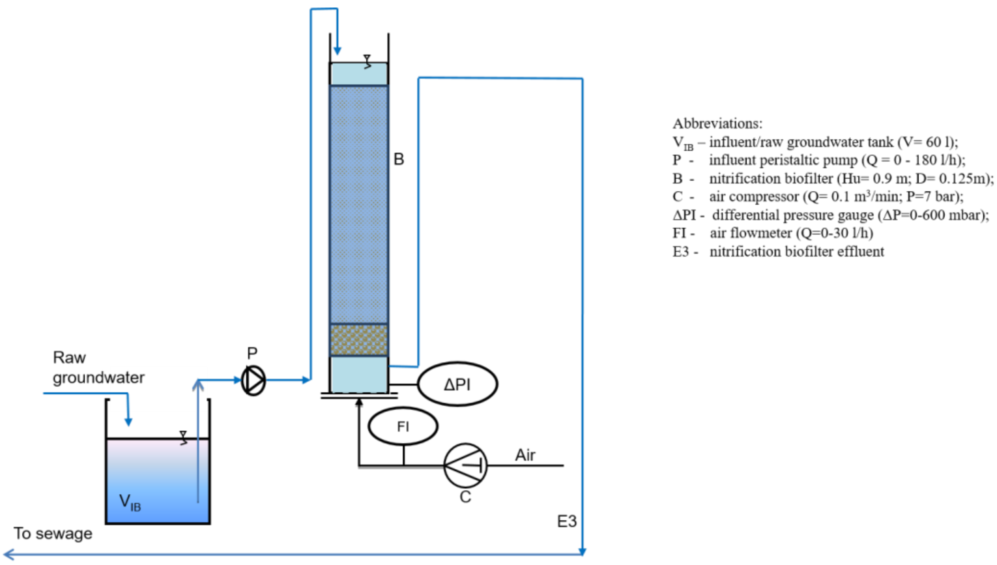

Figure 51. Pilot nitrification installation including a downflow biofilter filled with immersed expanded clay

The three bioreactors operated simultaneously, fed with raw groundwater with high concentration of ammonium, from source S1 (pH=7.73–8.84, alcalinity = 277-341 mg HCO_3^-/L, PO_4^{3-}=0.65-1.53 mg/L, NH_4^+=2.91-5.21 mg/L, NO_3^-< 0.1 mg/L, NO_2^-< 0.1 mg/L).

The nitrification performance of the three nitrification biological reactors experimentally tested was proven by the volumetric ammonium removal (oxidized) rate:

$$r_V = \frac{Q_{in}(S_{in}-S_{ef})}{V_b} \qquad (87)$$

where:

r_V - ammonium removal rate, g NH_4^+- N/m^3 filter media/day;
Q_{in} – influent flow, m^3/day;
S_{in} - concentration of NH_4^+- N in influent, mg/L;
S_{ef} - concentration of NH_4^+- N in effluent, in a pseudo-stationary state, for each applied load, mg/L;
V_b - filter media volume, m^3.

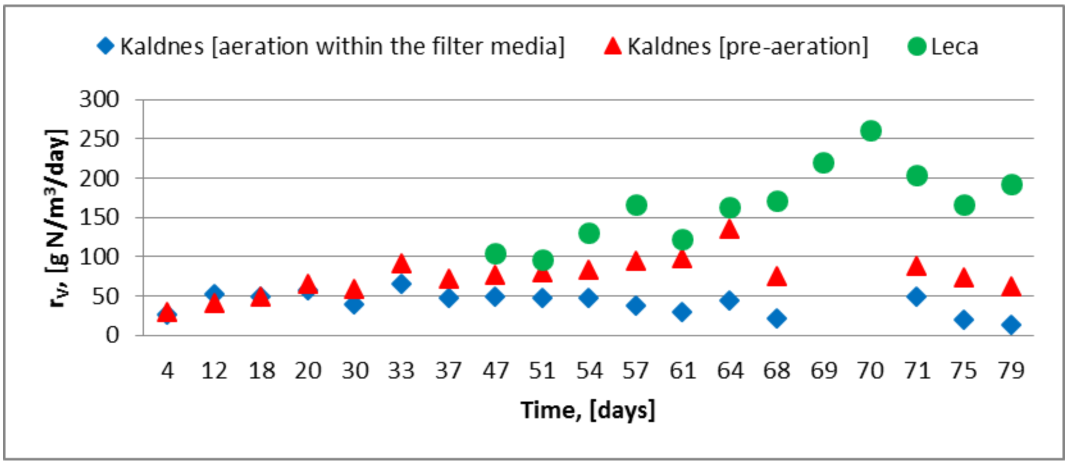

Figure 55. Comparative ammonium removal rates in aerated bioreactors, with different filter media and with different hydrodinamical configurations

Figure 55 presents comparatively the ammonium removal rates resulted in the three nitrification pilot installations.

In the upflow Kaldnes media bioreactor with aeration in the bed, ammonium removal rates were obtained ranging from 13 - 66 g N/m^3 media/day, including the startup period, the explanations for the lower rates of nitrification would be that the smooth surfaces of the media do not facilitate the adhesion of the biofilm, and the aeration within the bed favours the loss of biomass with the effluent. Residual concentrations of NH_4^+ in the effluent were, with some exceptions, over the limit of 0.5 mg/l, revealing the fact that loads exceeding the nitrification capacity of the biofilter were used. Washing the biofilter is not required due to the increased void fraction (67%) and their large size.

In the upflow Kaldnes media bioreactor with the pre-aeration of the influent and effluent recirculation, higher ammonium removal rates were obtained in the range of 30-135 g N/m^3 media/day, including the startup period, the explanation for the relatively low ammonium removal rates, but almost double to those obtained in the bioreactor with Kaldnes media being that the smooth surfaces of the media do not facilitate the adherence of the biofilm, but avoiding aeration in the bed, with the price of recirculation, in order to ensure the oxygen amount necessary to the biochemical reactions is advisable. Residual concentrations of NH_4^+ in the effluent were, with some exceptions, over the allowed limit of 0.5 mg/l, revealing that one has worked with loads exceeding the nitrification capacity of the biofilter. Washing the biofilter is not required due to the high void fraction (67%) and their large size.

In the bioreactor with expanded clay, grain size of 4-10 mm, with downflow of influent and aeration within the bed, nitrification rates were obtained in the range of 97-261 g N/m^3 media/day, including the startup period, the explanation for the higher rates than those obtained in the upflow bioreactor with Kaldnes media and with the pre-aeration of the influent and effluent recirculation would be that surfaces with pores of the granular mineral media facilitates the attachment of biofilm and provides a larger area for its development. Residual concentrations of NH_4^+ in the effluent were, with some exceptions, over the admitted limit of 0.5 mg/l, revealing the fact that one has worked with loads exceeding the nitrification capacity of the biofilter. At higher levels of water in the biofilter with 0.5 m, the biofilter was washed according to the following sequence of operations: breaking up with air for 5 min., at a filtration rate of 40-50 m/h; washing with water and air in co-current flow for 5 minutes at a filtration rate of 20-25 m/h for water and 40-50 m/h for air; rinsing with water for 10 minutes at a filtration rate of 20-25 m/h.

Experiments for the selection of a recomanded biofilter media for the nitrification of raw groundwater, characterized by low organic carbon loads (so-called “pure” nitrification), led to the following conclusions

- development and fixing of nitrification bacteria on the media with smooth surfaces of the Kaldnes type are sensitive to the hydrodynamic conditions from the reactor, turbulences (for example, those created by the aeration within the bed), favoring the detachment of the biofilm and its loss with the effluent, with negative impact on the ammonium removal rate;
- the granular mineral media type expanded clay is more suitable for the “pure” nitrification than the Kaldnes tpye media, due to its larger specific surface and of the advantage offered by the surfaces with pores in relation to those with smooth surfaces when fixing and developing the biofilm;
- due to the greater nitrification rates, in order to conduct the ulterior nitrification experiments, expanded clay was chosen as the biofilter media.

7.2 NITRIFICATION EXPERIMENTS FOR SELECTING THE OPTIMUM GRANULOMETRIC FRACTION OF THE BIOFILTER MEDIA

After selecting the suitable filter media for the nitrification process of the raw groundwater sources, which was the expanded clay type of granular material characterized by a rough surface with macro-pores favouring the attachment of nitrifying bacteria, the next step is to select a granulometric fraction of expanded clay ensuring the highest nitrification rate, which would lead to the minimization of the reaction volume, but which would also allow an easy handling and which would minimize the particle loss at the washing of the biofilter.

Two pilot lab installations were tested within the experiment, each of them having an aerated biofilter equipped with expanded clay from one of the granulometric fractions of 2-5 mm and 4-10 mm, characterized in Chapter 6, and operated in the upflow mode, at the following parameters:

-biofilter with fraction of 2-5 mm: t = 9.8-17.8ºC, dissolved oxygen = 3.2-8.3 mgO_2/L, empty bed contact time= 4.3-7.4 min., filtration rate= 4.45-7.63 m/h;

-biofilter with fraction 4-10 mm: t =10.8-17.2ºC, dissolved oxygen =4.5-8.2 mgO_2/L, empty bed contact time = 4.4-13 min., filtration rate =1.96-6 m/h;

The two biofilters operated simultaneously, fed with raw groundwater with high concentration of ammonium from source S1 (pH=7,80–8,49, alkalinity = 275-335 mg HCO_3^-/L, PO_4^{3-}=0.47-1.5 6 mg/L, NH_4^+ = 2.20-6.156 mg/L, NO_3^-< 0.16 mg/L, NO_2^-< 0.16 mg/L).

The nitrification performance of the two aerated biological filters experimentally tested was expressed by the ammonium removal (oxidized) rate expressed by the equation (87), where S_{ef} is the sum of the concentrations N-NH_4^+ și N-NO_2^- in the effluent, and is presented in Figure 59.

The rates of the complete nitrification ($NH_4^+ \rightarrow NO_3^-$) obtained in the expanded clay bioreactor, granulometric fraction of 2-5 mm, were in the range of 180 – 305 g N/m^3/day, while the complete nitrification rates obtained in the expanded clay bioreactor, granulometric fraction 4-10 mm, were of only 83-211 g N/m^3/day. The comparative analysis of these results shows that the expanded clay, fraction 2-5 mm, used as an inert biofilter media led to obtaining ammonium removal rates higher with 15-180 % (in 80 % of the cases higher with 50-125%) than the expanded clay, granulometric fraction 4-10 mm.

The explanation lies in the greater specific surface area of granulometric size 2-5 mm.

The residual ammonium concentrations in the effluent were generally larger than the allowed limit of 0.5 mg/L, because greater ammonium loads were used than the nitrification capacity of the biofilters, the purpose of the experiments being that of determining the maximum nitrification speeds obtained with the two granulometric fractions.

Also, Figures 60-62 show the evolution of the ammonium, nitrate and nitrite concentrations, with the height of the expanded clay bed, granulometric fraction 2-5 mm. It is observed that as the water flows through the granular bed, the ammonium concentration decreases and the nitrate concentration increases with the height of the bed travelled.

These results were obtained in the conditions of biofilter washing with a frequency of once/week and a duration of 10 minutes, at the following parameters:

- air filtration rate of 60 m/h and water filtration rate of 35 m/h, for the fraction 2-5 mm;
- air filtration rate of 60-70 m/h and water filtration rate of 50-55 m/h, for the fraction 4-10 mm.

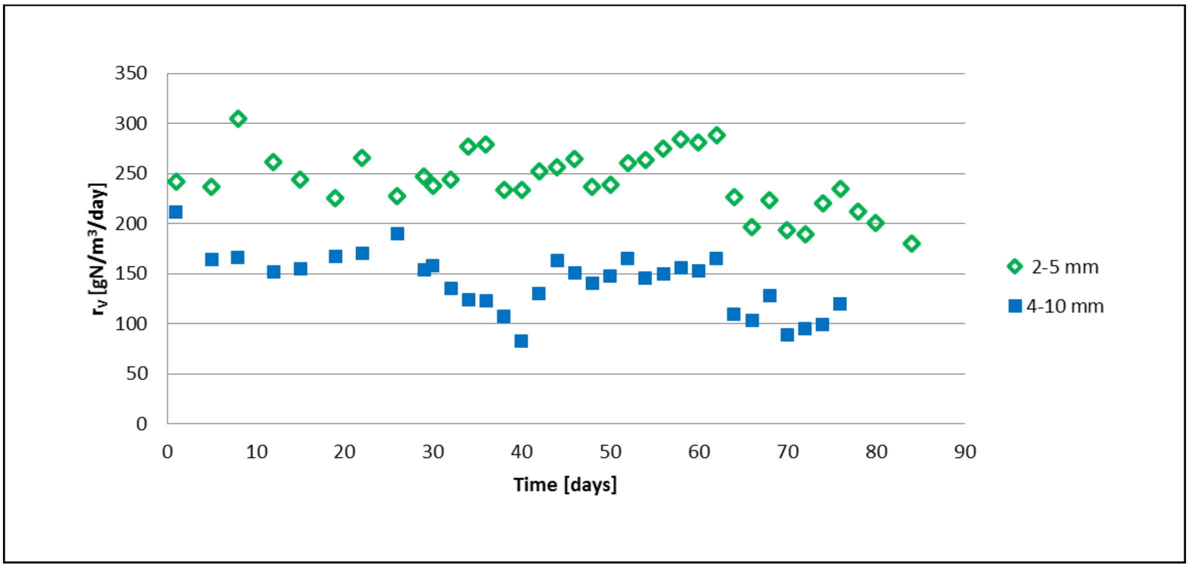

Figure 59. Comparative representation of ammonium removal rates for the aerated biological filters filled with expanded clay filter media, fractions 2-5 mm and 4-10 mm

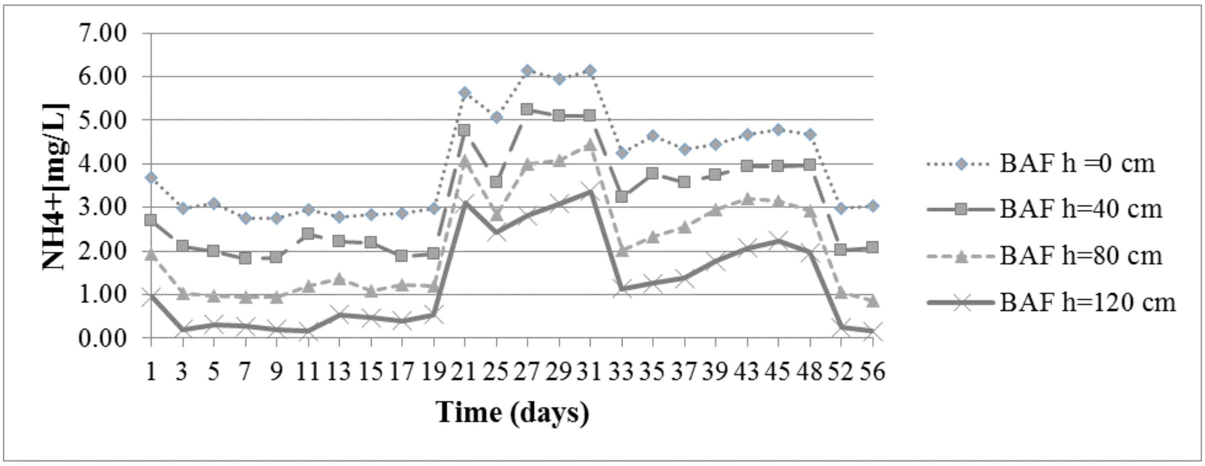

Figure 60. Evolution of the ammonium concentration in the biofilter filled with expanded clay, granulometric fraction of 2-5 mm

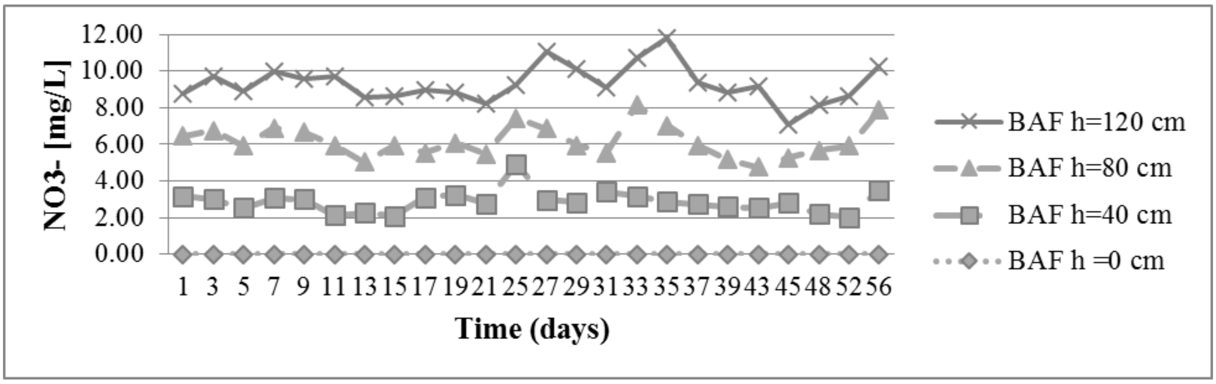

Figure 61. Evolution of the nitrate concentration in the biofilter filled with expanded clay, granulometric fraction of 2-5 mm

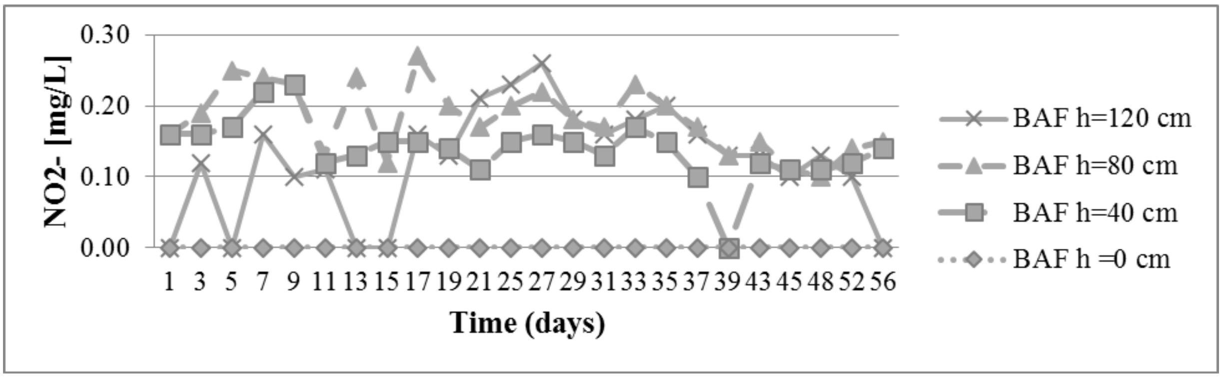

Figure 62. Evolution of the nitrite concentration in the biofilter filled with expanded clay, granulometric fraction of 2-5 mm

The conclusion in sub-chapter 7.1 was re-confirmed experimentally, and that is that the use of an ordinary and cheap granular material, such as Leca Laterlite^{TM} as filter media, results in some reasonably high nitrification rates.

The use of a smaller granulometric fraction as filter media leads to the possibility of obtaining greater biological response rates than those obtained with a higher fraction, due to the higher specific surface that allows the accumulation of larger biomass concentrations. The differences in reaction rates can be significant if the difference in dimension is significant, such is the case in this experiment. Higher reaction rates mean smaller size of bioreactors, so lower investment costs.

As a result of the experimental results, it was considered that the expanded clay fraction of 2-5 mm is the optimum choice for the nitrification process of groundwaters and is to be used in the ulterior nitrification experiments to determine the nitrification parameters.

7.3 EXPERIMENTS DETERMINING THE NITRIFICATION PERFORMANCE

As previously shown, the speed of the nitrification process is influenced by many factors in relation to the nitrifying bacteria parameters, the properties of the filter media, raw water characteristics and of the operating parameters of the biofilter. Determining the suitable filter media, the preliminary research stage previously described, removes from discution the first two categories of influence factors.

Some of the raw groundwater properties, mainly, the ammonium concentration and temperature, are data that cannot be altered and which are independent variables of the process, the other important nitrification characteristics, such as the anorganic carbon content/bicarbonate alkalinity and the phosphorus content necessary for bacteria growth usually being in sufficient amounts or having the possibility to be corrected.

Out of the operating parameters of the biofilter significant for process economy are the dissolved oxygen content and water - biofilm contact time. Usually, one uses sufficiently high dissolved oxygen concentrations to ensure that it does not become a rate-limiting factor, and the contact time for a particular type of filter media is a function of two parameters: filtration rate and the height of the bed. If setting the filtration rate at a value in the range recommended in the literature is made, then the ammonium, nitrite and nitrate concentrations in the biofilter are established according to the temperature, ammonia concentration in the influent and the height of the bed.

Reversing the reasoning and imposing restrictions to the ammonium and nitrite concentrations in the effluent at the regulated values of 0.5 mg/L and 0.1 mg/L, the height of the bed where this occurs becomes a function of two independent variables: temperature of the influent and the ammonia concentration in the influent at given values of the filtration rate. This way of approach allows the pre-sizing of the nitrifying biofilter in a particular given case.

The nitrification experiments already planned for this final stage aimes to achieve the following objectives:

- defining the co-dependent relation between the nitrification rates and the raw groundwater temperature at given values of the filtration rate and height of the bed;
- defining the co-dependent relation between the necessary height of the biofiltering layer to reach MACs imposed for ammonium and nitrite in the drinking water and the parameters of the raw groundwater – temperature and ammonium concentrations, at given values of the filtration rate.

7.3.1 Nitrification experiments for defining the dependence between the nitrification rate and the source temperature

The nitrification experience for identifying the co-dependent relation between the nitrification speed and reaction temperature have been performed at two apparent filtration rates: 10 m/h, recommended in literature for nitrification in granular media biofilters, and 5 m/h, for increasing the concentration range of ammonium in the influent.

In order to study the co-dependent relation of nitrification rate from the source temperature, synthetic influents have been used for the pilot nitrification installation, obtained by adding ammonium in the raw groundwater from a shallow source from Bucharest. The characteristics of the influents used in the pilot installation for the two filtration rates, 10 m/h (used as 10 mph below) and 5 m/h (used as 5 mph), are:

-for 10 mph: pH=6.82–7.24, alcalinity = 357-532 mg HCO_3^-/L, PO_4^{3-}=0.39-0.73 mg/L, NH_4^+=2.26-7.30 mg/L, NO_3^-< 0.1 mg/L, NO_2^-< 0.1 mg/L, Mn≤ 50 µg/L, Fe≤ 200 µg/L, TOC=3.7-5.9 mg/L;

-for 5 mph: pH=7.01–7.43, alcalinity = 332-445 mg HCO_3^-/L, PO_4^{3-}=0.55-0.89 mg/L, NH_4^+=8.55-23.20 mg/L, NO_3^-< 0.1 mg/L, NO_2^-< 0,1 mg/L, Mn≤ 50 µg/L, Fe≤ 200 µg/L, TOC=4.5-7 mg/L.

A pilot lab installation was used in the experiment (Figure 63), comprising one aerated biofilter, equipped with expanded clay of 2-5 mm granulometric fraction, operated in the upflow mode, at the following parameters:

-for 10 mph: t=10.2-22.8°C, dissolved oxygen=3.4-5.2 mgO_2/L, empty bed contact time =4.44-4.61 min., filtration rate =9.94-10.32 m/h;

-for 5 mph: t=11-25.2°C, dissolved oxygen =2.5-4.1 mgO_2/L, empty bed contact time =8.35-9.50 min., filtration rate =4.65-5.29 m/h;

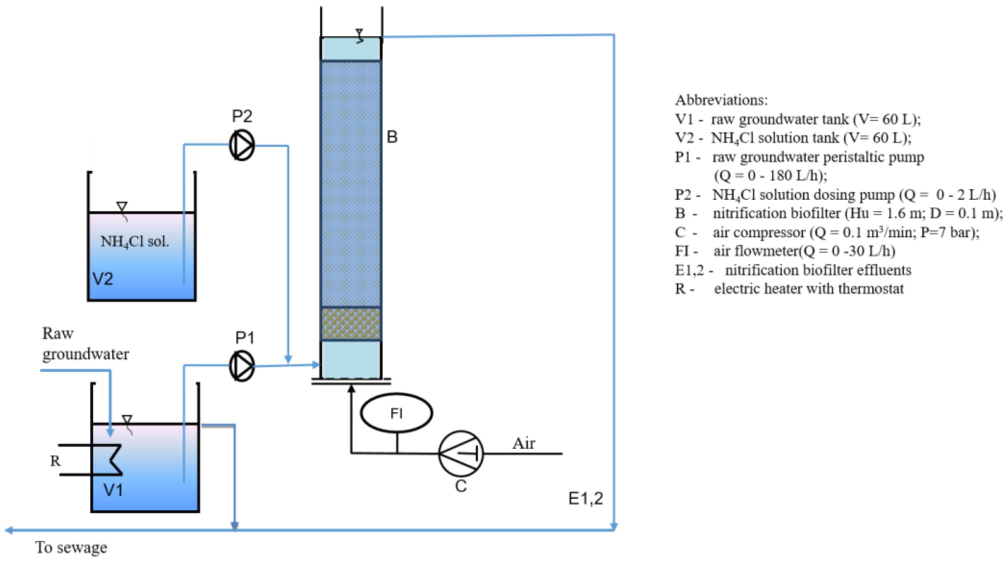

Figure 63. Pilot nitrification installation using an upflow aerated biofilter filled with expanded clay filter media, granulometric fraction 2-5 mm

The nitrification performance in the two experiments was expressed through ammonium removal rate expressed by equation (87), where S_{ef} is the sum of concentrations of NH_4^+- N and NO_2^--N in the effluent, graphically presented in Figures 66 and 67.

The nitrification rates obtained in the bioreactor using expanded clay of the granulometric fraction 2-5 mm have ranged between 353 – 819 g N/m^3/day for filtration rate of 10 m/h and 515-1337 g N/m^3/and for the filtration rate of 5 m/h, at temperatures varying in the range of 10.2 – 22.8 °C and, respectively, 11 – 25.2 °C.

The quality parameters of effluents, ammonium and nitrite have ranged within the MACs, here and there exceeding the MACs, especially for the nitrite.

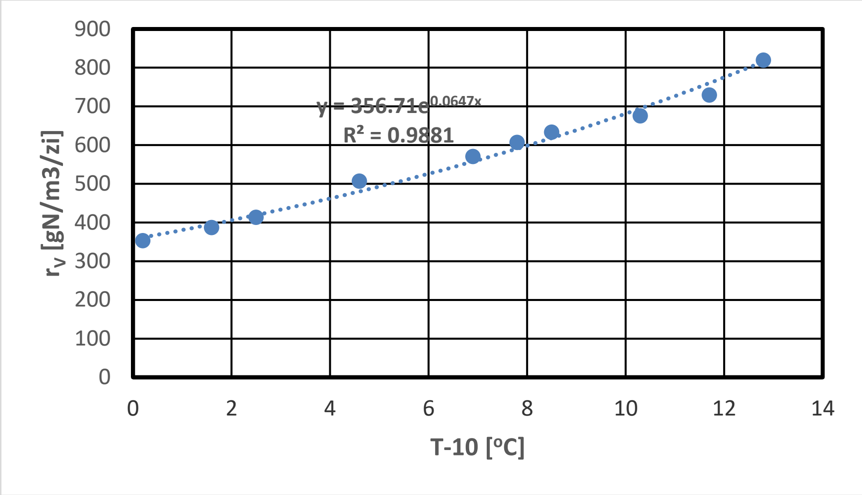

Figure 66. Nitrification rate vs. source temperature, w_f = 10 m/h

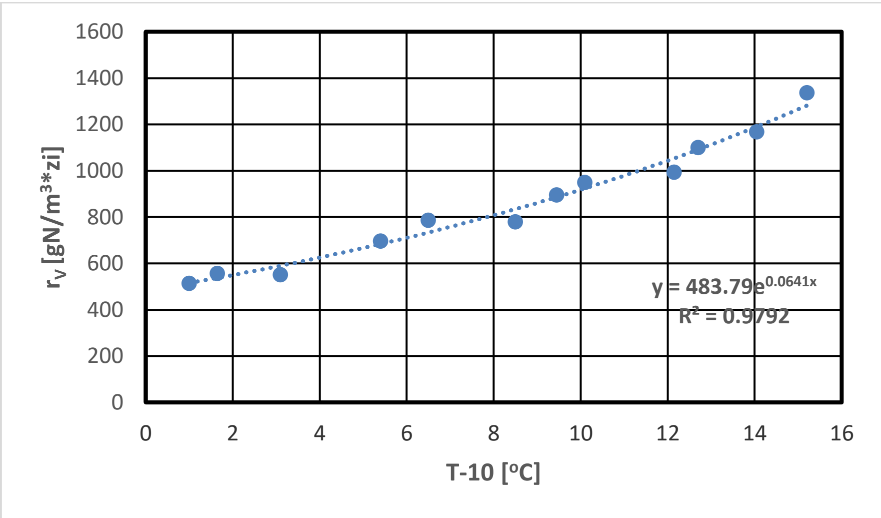

Figure 67. Nitrification rate vs. source temperature, w_f = 5 m/h

These results were obtained when washing the biofilter with a frequency of once/week and a duration of 10 minutes, at parameters of: air filtration rate de 55 - 60 m/h, water filtration rate of 30 - 35 m/h.

Mathematical processing of the obtained results was performed through the method of the smallest squares to obtain the following relations:

-for apparent filtration rate of 10 m/h:

$$r_V = 365.71\, exp^{0.0647(T-10)} \qquad (88)$$

-for apparent filtration rate of 5 m/h:

$$r_V = 483.79\, exp^{0.0641(T-10)} \qquad (89)$$

where:

r_V – nitrification rate, gN/m^3/day;

T - reaction temperature, °C.

For these dependencies, the values of the determining parameters were:

-R^2 = 0,9881, for the equation (88);

-R^2 = 0,9729, for the equation (89).

The experiments showed that by using the aerated biofilters equipped with expanded clay of granulomatric fraction of 2-5 mm and operated in upflow mode, one can obtain higher nitrification rates, comparable to those reported in specialized literature.

Through mathematical modeling of the dependent relation between nitrification rate and reaction temperature at two filtration rates of 10 m/h and of 5 m/h, resulted in temperature parameter of the same value, of 0.064/°C.

The values of determination coefficients close to 1, indicates a strong dependency of the nitrification speed and reaction temperature of the influent, which means that, under the circumstances of the experiment, other parameters did not significantly affect the results.

Higher nitrification rates obtained with the filtration rate of 5 m/h, is due to the higher water-biofilm contact time and the higher ammonium concentration applied.

The obtained results enable the predimensioning of the nitrification biofilters, if we know the temperature and the ammonium concentration of the raw water source and if the same biofilter media and operating parameters are applied to one of the two experimental cases.

7.3.2 Nitrification experiments for defining the dependence between the height of the filter media bed and the source parameters

Nitrification experiments for defining the dependence of the height of the filter media bed to the raw groundwater source parameters - temperature and ammonium concentration- were conducted at two filtration rates: 10 m/h and 5 m/h, the pilot plant being the one shown in Figure 63, operated at the parameters presented in section 7.3.1 and fed with synthetic influents constituted by adding ammonium in the supply flow of raw groundwater from a shallow source from Bucharest, with the characteristics listed in section 7.3.1.

Figures 68 and 69 show the results experimentally obtained - ammonium concentrations at different temperatures and heights of the bed.

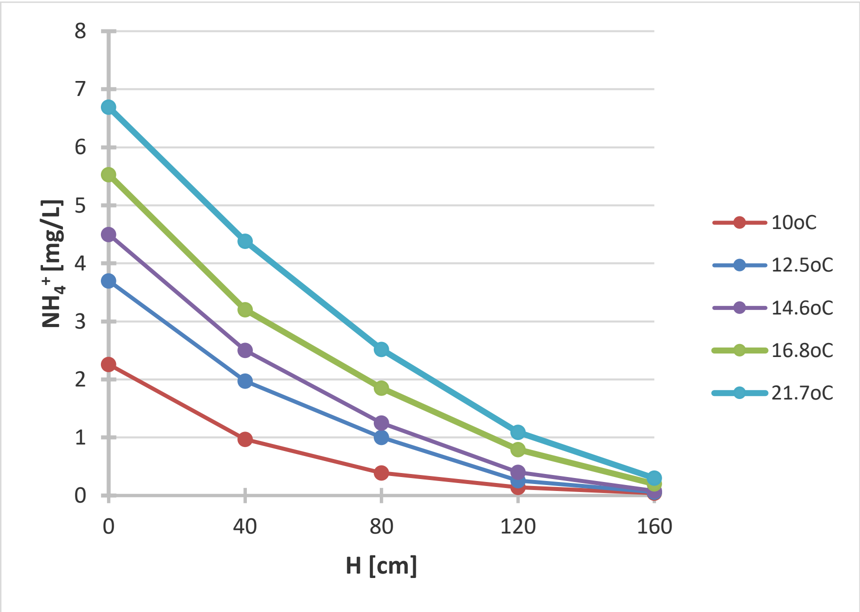

Figure 68 Variation of the ammonium concentrations with temperature and height of the biofiltering layer, w_f = 10 m/h

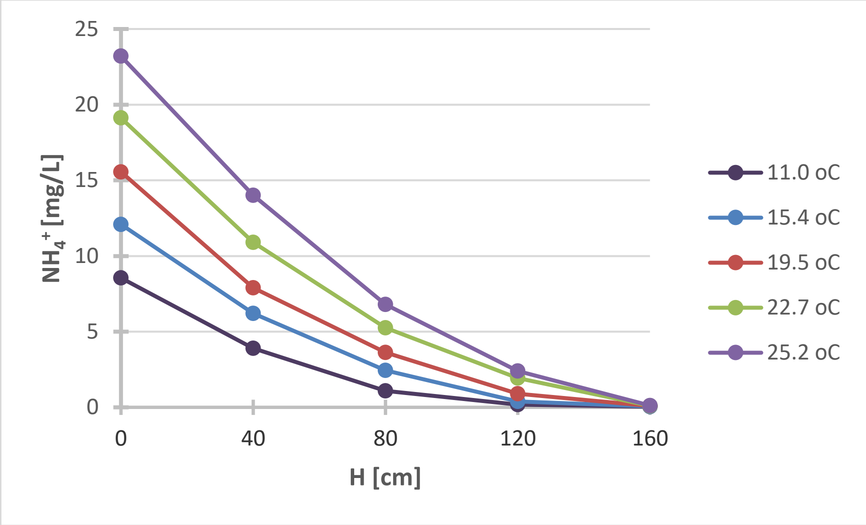

Figure 69. Variation of the ammonium concentrations with temperature and height of the biofiltering layer, w_f = 5 m/h

Quality parameters of effluents, ammonium and nitrite, have not exceeded the maximum allowable concentrations for drinking water, of 0.5 mg / L, respectively, 0.1 mg / L.

The biofilter washing was performed with a frequency of 1 time / week and lasted for 10 minutes, at the parameters: air filtration rate of 55-60 m / h, water filtration rate of 30-35 m/ h.

The correlation equations obtained using 3D TableCurve software (*30 Days Trial Version*) for the two cases, 10 mph and 5 mph, are of Chebyshev polynomial form with two variables:

$$z = a + bT_1(x') + cT_1(y') + dT_2(x') + eT_1(x')T_1(y') + fT_2(y') + gT_3(x') + hT_2(x')T_1(y') + iT_1(x')T_2(y') + jT_3(y') + kT_4(x') + lT_3(x')T_1(y') + mT_2(x')T_2(y') + nT_1(x')T_3(y') + oT_4(y') \quad (90)$$

where:

x- biological reaction temperature, °C;

y- ammonium concentration, mg NH_4^+/L;

z- height of the bed/biofiltering layer, m;

x_i'- coded value of the variable x, given by the relation:

$$x_i' = \frac{2\ln x_i - (\ln x_i)_{max} - (\ln x_i)_{min}}{(\ln x_i)_{max} - (\ln x_i)_{min}} \quad (91)$$

y_i'- coded value of the variable y, given by the relation:

$$y_i' = \frac{2\ln y_i - (\ln y_i)_{max} - (\ln y_i)_{min}}{(\ln y_i)_{max} - (\ln y_i)_{min}} \quad (92)$$

$$T_n(x') = \cos(n \arccos(x')) \quad (93)$$

$$T_n(y') = \cos(n\, arccos(y')) \quad (94)$$

The results of the correlation consisted of a-o coefficients' determining of equation (90) for the two cases, 10 mph and 5 mph, and in the response surfaces presented in Figures 70 and 71. The maximum residual values are of -9.366532% for 10 mph and of -5.756412% for 5 mph, and the average relative deviations (ARD) are of 1.3581% for 10 mph and of 1.0968% for 5 mph, which show that equations which correlate very well the experimental data were obtained.

A quantitative investigation of the influence of two independent parameters was performed, namely temperature and ammonia concentration, upon the height through sensitivity analysis, by Monte Carlo simulation, by using the Crystal Ball software, contributions being of -80% for the ammonia concentrations and of + 20% for the reaction temperature, for 10 mph, and of -83,5% for the ammonia concentration, and + 16.5% for the reaction temperature, for 5 mph. It can be seen that the most significant parameter is the ammonium concentration in the influent, the negative value of the sensitivity indicating a reverse proportionality.

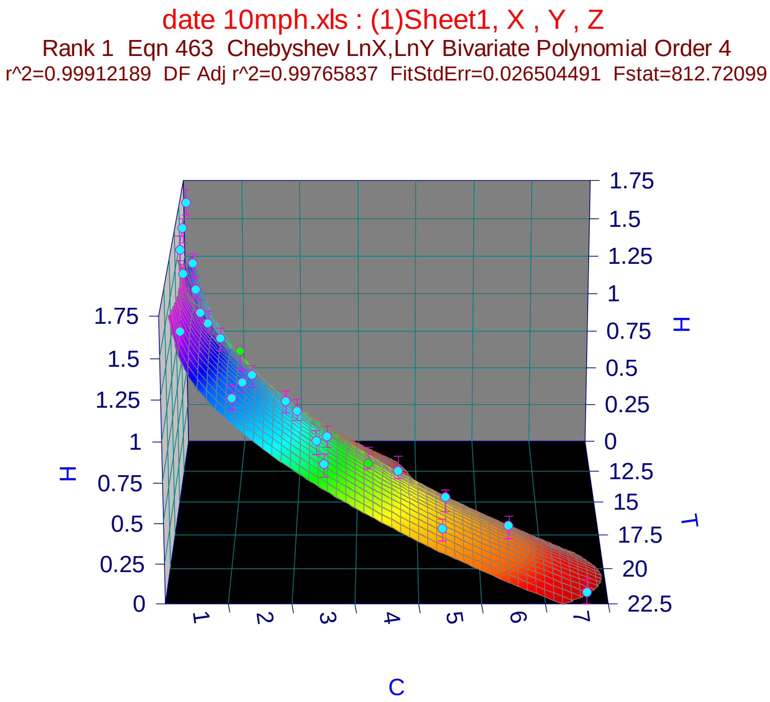

Figure 70. The variation of the height of the biofiltering layer with ammonium concentration and temperature, w_f = 10 m/h

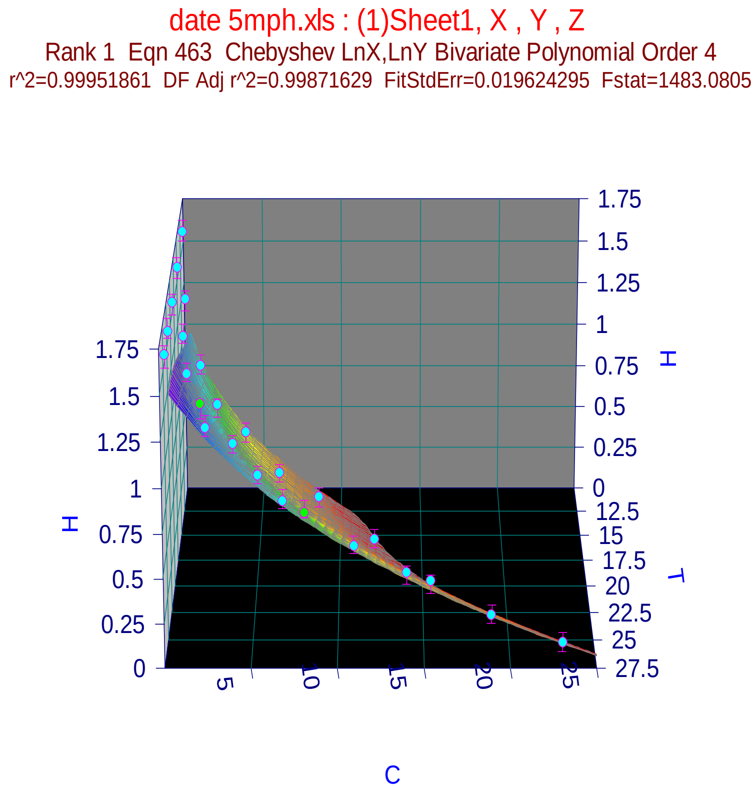

Figure 71. The variation of the biofiltering layer height with ammonium concentration and temperature, w_f = 5 m/h

The results make it possible to pre-size the nitrifying biofilters in condition that the temperature and the ammonium concentration of the raw water source are in the researched ranges and the same filter media is adopted and operating parameters are complied with the similarity criteria of one of the two experiments performed, with the equation:

$$h = 1{,}6 - z \quad (95)$$

where:
h – the necessary height of the bed to reach MACs for ammonium and nitrite in the drinking water, for a given temperature and ammonium concentration of the source, m;
z – the layer height, correspondent to the temperature and ammonium concentration of the raw water source, calculated with equation (90), m.

CHAPTER 8: GENERAL CONCLUSIONS, ORIGINAL CONTRIBUTIONS AND PERSPECTIVES FOR LATER DEVELOPMENTS

8.1 GENERAL CONCLUSIONS

For the development of the technology for the treatment of raw groundwater in view of making it potable, the paper includes complex research, including:
- analytical characterization of raw groundwater for drinking purposes;
- characterization of inert media to equip the nitrification biofilters;
- discover the main implications for the presence of ammonium in the raw groundwater on the treatment flows;
-researches on the nitrification process itself.

From the research concerning *the analytical characterization of raw groundwater intended to human consumption*, the following conclusions resulted:

- the raw groundwaters *intended to* human consumption of 11 locations from four counties of Romania (Ilfov, Călărași, Vrancea and Gorj), selected as a result of problems in treatment flows and quality non-compliances of drinking water supplied to consumers, were characterized through standardized methods and with modern analytical equipments,;
- *the common feature of the raw groundwater researched on, is the presence of ammonium ions in concentrations up to 7.4 mg NH_4^+/L, higher than the maximum allowed concentration (MAC = 0.5 mg / L) for all sources, which means that this issue is prevalent enough to require a systematic approach and whose proper solving depends essentially on the chlorine disinfection efficiency, indispensable step to any treatment flow*;
- there are frequent exceedings of the maximum allowed concentrations for the indicators Mn (MAC = 50 µg/L) – concentrations of up to 230 µg/L in 73% of the investigated locations, and Fe (MAC = 200 µg/L) – concentrations of up to 8400 µg/L in 73% of the investigated locations to consider when establishing the treatment flows;
- for sources S1 and S2 it has been found that hardness is below the allowed limit (5 German degrees), which, although do not pose health problems, must be corrected for conforming reasons.

The paper established the main *implications of ammonium ions in raw groundwater over the treatment flows,* and that is:

- ammonium must be removed before the disinfection stage because it compromises it through the fact that it reacts with the chlorine destined for its disinfection;
- in theory, the ammonium removal from water can be obtained chemically, through chlorination at the breakpoint, chlorine being the only reagent capable of completely oxidize the ammonium;
- chlorination at the breakpoint requires high mass ratios Cl_2 : N-NH_4^+ (minimum 8:1), which means high reagent consumptions, with the afferent costs, and reaction times of 30-40 min.;
- the ammonium oxidation with chlorine implicitly implies introducing chloride ions in the drinking water;
- at high ammonium concentrations, a decrease of the pH takes place through chlorination, being necessary to correct this decrease, which means using other reagents, with the afferent costs, and the introduction of ionic species in the drinking water;
- chlorine results from the ammonia oxidation, resulting secondary by-products of reaction, trihalomethanes and chloramines, and these being regulated due to their toxicity;
- the quantity of secondary products depends on multiple factors, among which the chlorine dose, determined at its turn by the ammonium concentration in the raw water;
- removing chloramines, and partially the trihalomethanes, can be achieved by granular activated carbon adsorption, at contact time of 4-8 min.;
- *always, the nitrification is the best solution for ammonium removal from raw waters meant for human consumption, applicable imperatively when ammonium concentrations exceed 1.5 mg/L;*
- at ammonium concentrations lower than 1,5 mg/L one can also use the complete chlorine oxidation (breakpoint oxidation), easier to implement in the existing treatment flows;
- when raw groundwater contain simultaneously ions of iron, manganese and ammonium, which are removed chemically, the order of removal is iron (air oxidation + sand filtration), manganese (Cl_2 or $KMnO_4$ oxidation, according to concentration, + manganesed sand filtration) and ammonium (oxidation with Cl_2 + filtration on granular activated carbon);
- when raw waters contain simultaneously manganese and ammonium and when nitrification is required, the order of removal is ammonium (nitrification), followed by manganese (chemical or biological removal).

The research conducted within the paper for *characterizing the types of inert media for the nitrification biofilters,* led to the following conclusions:

- considering the properties of bacteria making the nitrification – poor surface adherence and slow growing rate – a granular mineral material was selected for the characterization, light expanded clay that when moist becomes heavier than water, whose properties were suitable for the process;
- from a commercial type of expanded clay of larger size, two granulometric fractions were separated, 2-5 mm and 4-10 mm, which were subjected to property testing – elemental analysis, leachate analysis, determining the physical and geometrical properties of grains and of granular layer;

- XRF analysis identified 18 component elements of the expanded clay material, quantitatively predominant being silicon (18,3 % gr.), aluminum (9.66 % gr.), iron (5,66 % gr), calcium (2,32 % gr.), manganese (1, 05 % gr.) and potassium (1,49 % gr);
- the leachate analysis confirmed the inert character of the material, the metal concentrations in the leachate being below the maximum values allowed in the drinking water;
- the research on the morphology of the surface grains revealed rough surfaces, with macro-pores of bacterial size or larger, where the nitrifying biofilm can develop;
- *physical and geometrical properties of the granulometric fraction of 2-5 mm (ε = 0,46; ρ_m = 820 kg/m^3; ρ_{bulk} = 440 kg/m^3; d10 = 2,3 mm, d50 = 3,1 mm) and of the granulometric fraction of 4-10 mm (ε = 0,50; ρ_{bulk} = 385 kg/m3; d10 = 4,6 mm) were determined, the two fractions being selected for conducting the nitrification experiments;*
- comparatively, except for the two granulometric fractions of expanded clay, a random plastic media was selected for the preliminary nitrification experiments made of individual bodies of plastic, with properties: ϕ x h = 16 x 9 mm, ρ_m = 750 kg/m^3, ρ_{bulk} = 250 kg/m, ε = 0,67, σ =750 m^2/m^3.

The paper presents the research regarding the *selection of the filter media type for the actual nitrification experiments*, and its main conclusions are as follows:

- the nitrification rates obtained with granular filter media of expanded clay were significantly higher (163-261 gN/m^3/day) than those obtained with a random plastic media made from individual bodies of plastic material (13-66 gN/m^3/day and 59-135 gN/m^3/day), bioreactors being operational simultaneously, fed with the same influent;
- the explanation is that the smooth surface Kaldnes type filter media does not favor the attachment of the nitrifying bacteria, the resulted biofilm being sensible to the hydrodynamic conditions from the bioreactor, turbulence (for example, those created by the aeration in the bed) favoring the biofilm detachment and its loss with the effluent, with impact on the nitrification rates;
- *the expanded clay granular filter media is more suitable for the "pure" nitrification than the Kaldnes type filter media , due to its large surface area and to the advantage offered by the macro-pores surfaces protecting the biofilm against shearing forces when operating and washing, being selected for the ulterior nitrification experiments*

Also, research was conducted regarding the *experimental selection of the granulometric fraction of expanded clay for the nitrification experiments,* which led to the following conclusions:

- the nitrification rates obtained with the granulometric fraction of 2-5 mm (180-305 gN/m3/day) were with 15-180% higher (with 50-125% higher in 80% of determinations) than those obtained with granulometric fraction of 4-10 mm (83-211 gN/m3/day);
- *the expanded clay of granulometric fraction 2.5 mm was selected for the actual nitrification experiments because it allows to obtain higher biochemical reaction rates, due to the larger surface area of the layer, compared to the fraction of 4-10 mm.*

The wide technological research on the nitrification process to *determine the dependence between the nitrification rate and the source temperature,* led to the following conclusions:

- the nitrification *rates* obtained in a upflow biofilter, equipped with expanded clay media of granulometric fraction of 2-5 mm with a height of 1.6 m, were situated in the range of 353 – 819 g N/m^3/day for the filtration rate of 10 m/h and 515-1337 g N/m^3/day for the filtration rate of 5 m/h, at temperatures ranging from 10,2 – 22,8 ^oC and, respectively, 11 – 25,2 ^oC;

- higher reaction *rates* obtained for the filtration rate of 5m/h were significantly higher than those obtained for the filtration rate of 10 m/h, due to the double time of water-biofilm contact and of the higher ammonium concentration gradient;
- the values obtained for the nitrification rate are high, considering we are talking about the "pure" nitrification stage;
- quality parameters of effluents, ammonium and nitrite, were within MACs, though registering some exceeding, especially for nitrite;
- the previously mentioned nitrification rates were obtained under the conditions biofilter washing with a frequency of once/week and with a duration of 10 minutes, at parameters: air filtration rate = 55 - 60 m/h; water filtration rate = 30 - 35 m/h;
- *the regression of the experimental data was conducted through the method of the smallest squares and led to exponential rate type equations (equations 88 and 89), with values similar to that of the temperature coefficient of about 0,064/^oC, for both filtration rate (10 m/h and 5 m/h) which were used;*
- the values of the determining coefficients close to 1 (R^2 = 0,9881 for 10 m/h and R^2 = 0,9729 for 5 m/h) indicates a strong relation between of the nitrification rate and reaction temperature of the influent, which means that, in the given conditions of the experiment, other parameters did not significantly influence the results;
- the results, obtained in the kinetics study of the nitrification process according to the temperature, are recommended to be used in the pre-sizing and evaluation of operating a nitrification biofilter in the same conditions;

Thorough experimental research was conducted on the kinetics of the nitrification process itself – *determining the dependence of the biofiltering height from the source parameters (temperature and ammonium concentration),* and the resulted conclusions were as follows:

- ammonium concentration fields were revealed in an upflow aerated biofilter, equipped with a layer of expanded clay fraction 2-5 mm, operated at two filtration rates (10 m/h and 5 m/h), depending on the height of the layer traveled by the influent (up to 1.6 m) and biochemical reaction/influent temperature (10 - 25.2 ° C)
- quality parameters of effluents, ammonium and nitrite, were below MAC values;
- the washing parameters of the biofilter were determined: frequency - 1 once/week; duration- 10 minutes; air rate = 55 - 60 m/h; water rate = 30 - 35 m/h;
- *through the mathematical modeling of the dependence of height from the parameters of the raw groundwater source - the temperature and the ammonium concentration - polynomial relationship were obtained, of the Chebyshev type (equation 90) and surfaces that describe this dependence for the filtration rates of 10 m/h and 5 m/h (Figures 70 and 71);*
- the average relative deviations were low - 1.3581% for the filtration rate of 10 m/h and 1.0968% for that of 5 m/h, hence the equations correlate very well the experimental data;
- a sensitivity analysis was performed, to investigate the quantitative influence of the two independent parameters, temperature and, respectively, the ammonium concentration in the influent, upon the height of the biofiltering layer and the resulting parameter which was the most significant, is the ammonium concentration in the influent, with an influence of -80 % regarding the filtration rate of 10 mph, and of -83.5% for the filtration rate of 5 mph, the negative value of the sensitivity indicating a reverse proportionality;

- the results are recommended to be used to sizing and evaluation of operating a nitrification biofilter according to temperature and ammonium concentration of the raw water source in the situation when the same filter media is adopted and when the similarity criteria from the one of the two case studies are respected.

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