Impact of Temperature on Groundwater Nitrification in an Up-Flow Biological Aerated Filter Using Expanded Clay as Filter Media

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*The temperature influence upon the nitrification rate was studied using a continuous flow pilot installation, which comprises a biological aerated filter with ascendant inflow circulation. Used filter media was expanded clay, 2-5 mm granulometric fraction. The biofilter was fed with raw low - depth groundwater enriched with NH_4^+. Inorganic nitrogen forms (NH_4^+, NO_2^-, NO_3^-) concentrations were measured both within the inflow and outflow of aerated biological filter, at stationary operation regimes in correspondence with various applied NH_4^+ loadings. Values of NH_4^+ removal rates were situated within the 515-1337 g NH_4^+-N/m^3*day domain for temperature increase from 11 to 25.2 ^{o}C. The coefficients of reaction rate vs. reaction temperature equation were also determined.*

Keywords: groundwater, nitrification, biological aerated filter, expanded clay, ammonium removal rate

Beside surface water, groundwater represents one of the two important European raw sources of water intended for human consumption [1]. Ammonium (NH_4^+) presence in sources of water intended for human consumption is not desired due to the fact that can perturb chlorine disinfection, which represents the final step of potabilization process for the majority of Romanian water treatment plants, can lead to taste and odour problems and can cause bacterial growth in drinking water distribution network [2].

Ammonium removal from water intended for human consumption, such as groundwater sources [3, 4], up to concentrations below maximum admissible concentration (0.5 mg/L) in Europe [5] and, implicitly, in Romania [6], can be done as a pre-treatment step in potabilization plants, mainly through two methods: breakpoint chlorination and biological nitrification.

Chemical method uses chlorine as oxidative agent, but its appliance is limited at ammonium concentrations lower than 1 mg/L, due to obvious and potential drawbacks [7]: high chlorine consumption, possible decrease of μH below the permitted value (*p*H = 6.5) and possible formation of trihalomethanes above the allowed limit (100μg/L).

Biological nitrification applicable for $NH4^+$ concentrations higher than 1 mg/L, consists in oxidation reactions chain $NH4^+ \rightarrow NO_2^- \rightarrow NO_3^-$, performed by autotrophic aerobic nitrifying bacteria, *Nitrosomonas sp.* and *Nitrobacter sp.* [8]. Among method's advantages can be mentioned: high nitrification efficiencies, avoidance of chemical reagents use for drinking water, a decrease of chlorine doses used for disinfection and low concentrations of trihalomethanes and chloramines in drinking water.

Biological nitrification of groundwater is close to so-called *pure nitrification culture* [9], due to organic carbon low concentration. In the absence of heterotrophic aerobic bacteria, nitrification bacteria present a weak adherence to surfaces. In order to favour nitrification bacteria fixation and growth there is a need for filtration media having a porous surface and a high specific surface area [10].

Nitrification of groundwater intended for potabilization is usually carried out in submerged biological aerated filters (BAF's), which use granular materials such as expanded clay as biofiltration media.

Biological nitrification process depends on many factors [11]: the characteristics of nitrifying bacteria (low growth speed, high sensibility to environmental conditions, poor surface adhesion), the reaction medium (water composition, *p*H, alkalinity, temperature) the filter media characteristics (type, size, porous surface, surface area) and the operation parameters of the bioreactor (dissolved oxygen concentration, filtration rate, contact time, washing parameters). Taking into account these factors, nitrification performances reported in literature in a wide range of values [12], are difficult to be generally applied and a specific case study is needed.

For example, ammonium removal rates for BAF varied between 0.25 - 0.6 kg NH_4^+-N/m^3 filter media/day, depending on the reaction temperature, contact time, type and effective size of filter media [13].

Experimental data regression, in order to obtain a mathematical equation that reflects the dependence between variables, can be obtained using least squares method [14].

The present work objectives were (1) to determine the ammonium removal rate from an underground water source at various reaction temperatures and (2) to calculate the reaction rate vs. temperature equation coefficients using an up-flow pilot scale BAF with expanded clay as filter media.

Experimental part

Nowadays, in Romania, nitrification and biological nitrification in particular, is not applied as pre-treatment step within potabilization plants, even if there is a need for such processes in some cases. Therefore, there is a lack of practical experience related to the design and operation of biological nitrification installations, any nitrification experiment that lead to knowledge improvement in the field being useful and welcomed.

Performed biological nitrification experiments had the following objectives:

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- to determine the ammonium removal rates at different reaction temperatures, using an up flow biological aerated filter with expanded clay granules as a filter media, for a certain value of filtration rate / contact time;

- to determine the coefficients of mathematical model that describes the dependence of ammonium removal rate on temperature.

In order to achieve these objectives, the following activities were performed:

- analytical investigation of low depth groundwater source in order to determine the variation domains of the main parameters of interest in a biological nitrification process: pH, NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}, alkalinity;

- continuous pilot scale biological aerated filter design and construction;

- inoculation of the inert granular filter media;

- bioreactor operation, in usual areas of operating parameters, with NH_4^+-N loadings corresponding to maximum nitrification capacity;

- inflow and outflow analytical investigation in order to determine NH_4^+, NO_2^-, NO_3^- concentrations;

- calculation of ammonium removal rate;

- assessment of the coefficients of mathematical model that describes the dependence between ammonium removal rate and temperature.

Materials and methods

The biological nitrification experiment was conducted in a continuous pilot scale biological aerated filter operated in up-flow mode (fig. 1). Low-depth groundwater enriched with NH_4^+ was the pilot installation inflow. The biological aerated filter with a diameter of 100 mm was filled with expanded clay granules to a height of 1.60 m.

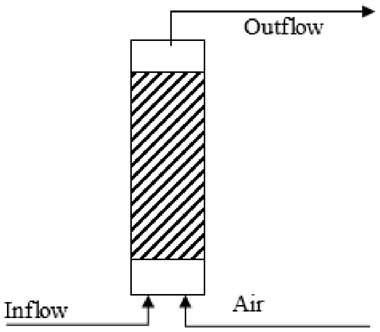

Fig. 1. Schematic of up-flow BAF

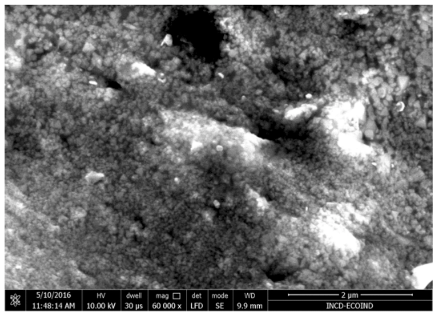

Fig. 2. Scanning electron micrograph of a Leca Laterlite™ granule

The expanded clay granules used as a filter media represented the 2-5 mm granulometric fraction of Laterlite™ Leca commercial assortment, obtained by sieving. The filter media characteristics are shown in table 1. Scanning Electronic Microscopy (SEM) micro-photo of expanded clay granule surface covered with biofilm is presented in figure 2.

After a period dedicated to inoculation of the expanded clay media, nitrification experiments were conducted at the operating parameters presented in table 2. Biofilter was washed once/week, for 10 min, with water and air flow rates corresponding to speeds of 25 - 35 m/h and 50 - 60 m/h.

The nitrification process evolution in the bioreactor was investigated by analytical methods that determined ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-) concentrations both in the inflow and outflow. Concentrations of previously mentioned inorganic nitrogen forms, as well as the phosphate ion (PO_4^{3-}) concentration were determined by ion chromatography using an ICS-3000 system (Dionex, USA), according to standard method SR EN ISO 14911 for ammonium, and SR EN ISO 10304/1:2009 for anions. Other parameters that were investigated were: concentration of inorganic carbon was determined as bicarbonate concentration (HCO_3^-) in accordance with standard method SR ISO 9963/1/A99:2002; dissolved oxygen (DO) concentration was measured with Oxi320 device, (WTW, Germany); *p*H and temperature were measured with C932 device, (Consort, Belgium);

Results and discussions

Assessment of groundwater quality

The analytical investigations revealed the concentration range of inflow's main quality parameters (table 3), highlighting the high concentration of ammonium ions

Granulometric fraction, [mm]	D10 diameter [mm]	Density, [kg/m^3]	Bulk density, [kg/m^3]	Porosity, [%]	BET surface area, [m^2/g]
2-5	2.3	815	440	46	0.71

Table 1
CHARACTERISTICS OF LECA LATERLITE™ MEDIA

Average temperature in BAF, [°C]	Dissolved oxygen in outflow, [mg/L]	Contact time, [min.]	Filtration rate, [m/h]
11.0 - 25.2	2.5 – 4.1	8.35 – 9.50	4.65 – 5.29

Table 2
OPERATING PARAMETERS FOR BAF

Parameter	Measurement unit	Domain	Permitted value by Romanian Law 458/2002, republished in 2011
pH	-	7.01 – 7.43	6.5 – 9.5
Alkalinity	mg HCO_3^-/L	332– 445	-
NH_4^+	mg/L	8.55 – 23.20	0.5
NO_3^-	mg/L	< 0.1	50
NO_2^-	mg/L	< 0.1	0.1
PO_4^{3-}	mg/L	0.55 – 0.89	-

Table 3
GROUNDWATER CHARACTERISTICS

(8.55 - 23.20 mg/L), far above the maximum admissible limit (0.5 mg/L).

Ammonium removal rate

Nitrification performance was calculated according to the following equation:

$$r_V = \frac{Q_{in}(S_{in} - S_{out})}{V_b} \quad (1)$$

where:

γ_V - ammonium removal rate, g NH_4^+-N/m^3 filter media/ day;

$Q_{\backslash in}$ - inflow flowrate, m^3/day;

S_{in} - inflow NH_4^+ - N concentration, mg/L;

S_{out} - pseudo steady state outflow NH_4^+-N concentration and NO_2^--N concentration sum for each loading condition, mg/L;

V_b - volume of filter media, m^3.

The ammonium removal rate varied between 515 – 1377 g NH_4^+-N/m^3 filter media day (fig. 3), for a filtration rate of about 5 m/h corresponding to a contact time of about 8.9 minutes and reaction temperature between 11 – 25.2 °C and by using expanded clay granules (2-5 mm) as a filter media.

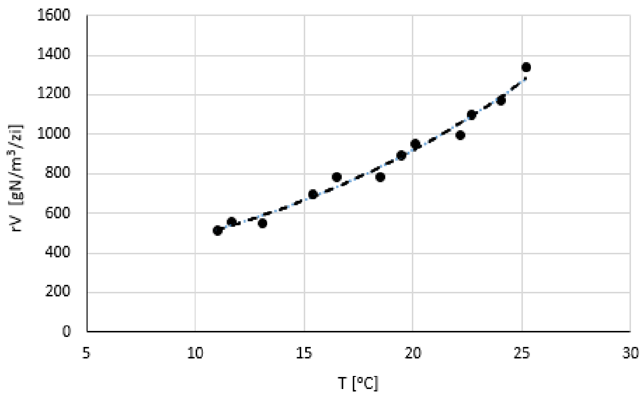

Fig. 3. Ammonium removal rate versus reaction temperature for BAF with 2-5 mm expanded clay as filter media, contact time ≈ 8.9 min.

During the experimentation period, ammonium inflow loads applied were situated close to BAF nitrification capacity and NH_4^+ and NO_2^- concentrations of the outflow did not exceed the imposed limits.

Mathematical model of nitrification rate dependence on reaction temperature

Least square method regression applied to experimental data led to the following equation:

$$r_V = 483.79\, e^{0.0641(T-10)} \quad (2)$$

where:

γ - ammonium removal rate, g NH_4^+-N/m^3 filter media/ day;

T - average reaction temperature, °C.

For the experimental data used in equation (2), the coefficient of determination had a value R^2 = 0.9792, which shows that almost 98% of ammonium removal rate variation was determined by reaction temperature variation.

Conclusions

Nitrification experiments were performed in a BAF with expanded clay as filter media, with up-flow water circulation. Low-depth groundwater enriched with ammonium was used as inflow. Biological nitrification reactions took place at temperature domain between 11-25.2 °C. Ammonium loads were applied at biofilter's nitrification capacity for a filtration rate of about 5 m/h and a contact time value of about 8.9 min.

Biological nitrification process was complete, residual concentrations of ammonium and nitrites being lower than 0.5 mg/ and 0.1 mg/L, respectively, at ammonium removal rates between 515 – 1377 g NH_4^+-N/m^3 filter media/day.

Least square regression method was used resulting an exponential dependence of the nitrification rate on temperature and coefficient of determination value was R^2 = 0.9792, indicating a good correlation between those two variables.

Presented nitrification experiment proved that biological nitrification of groundwater with high ammonium content using BAF's filled with expended clay, with up-flow water circulation, is an efficient pre-treatment process for drinking water.

Obtained nitrification rate vs. temperature equation constitute a useful practical tool for design of BAF for nitrification of groundwater with high ammonium content.

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