Nitrification Front Evolution in a Biological Aerated Filter Using Expanded Clay As a Filter Media

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A pilot scale biological aerated filter (BAF) was built in order to test the ammonium removal from a groundwater source intended for drinking water. Expanded clay granules were used as a filter media. In order to study the conversion rates of various ammonium loads, a pollutant present in groundwater, the up-flow bioreactor was divided into three equal size sectors. The evolution of inorganic forms of nitrogen (NH_4^+, NO_2^-, NO_3^-) concentration fronts along the height of the filter media and the ammonium removal rates were determined.

Keywords: groundwater, nitrification, biological aerated filter, expanded clay

Groundwater is an important source of drinking water, in Europe, where it represents almost 50% of consumption [1], as well as in Romania. Water pollution with nitrogen compounds above the admissible limits can lead to environmental (lack of oxygen, eutrophication, aquatic toxicity) and public health issues like bad taste and odor of the drinking water and methemglobinemia (blue baby syndrome) [2]. Ammonium presence in potable water sources, especially groundwater [3, 4], over the maximum allowable concentration (0.5 mg/L) normed by both European Union regulations [5] and also by the national legislation [6], requires its removal.

Ammonium removal from water intended as drinking water can be done by using a common chemical method - breakpoint chlorination, when chlorine and ammonium concentrations are simultaneously minimized, chlorine being the only oxidizing agent that can react with ammonium at natural water's *p*H. This method is not recommended for ammonium concentrations higher than 1 mg / L due to the following disadvantages [7]: high chlorine consumptions, high bound/free chlorine ratio, possible decrease of pH below the permitted value (*p*H = 6.5), development of chlorination byproducts (eg. trihalomethanes, THMs) over the allowed limit (100 μg/L), if the water contains reactive-to-chlorine natural organic matter such as humic substances.

For waters with concentrations higher than 1 mg/L, ammonium removal is recommended to be done by biological oxidation ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$), performed by autotrophic aerobic nitrifying bacteria, *Nitrosomonas sp.* and *Nitrobacter sp.* [8]. This method offers important advantages such as: high efficient bio-oxidation, a decrease of chlorine doses used for disinfection and low concentrations of trihalomethanes and chloramines in drinking water.

Nitrification of waters intended for potabilization or for quality polishing is usually carried out in biomass attached reactors [9] like: rotating biological contactors, nitrifying trikling filters (NTF's) and submerged biological aerated filters (BAF's).

Due to the different nature of extracellular polymeric substances (EPS) synthesized by autotrophic nitrifying bacteria and heterotrophic bacteria [10], flocculation and adhesion to surfaces characteristics of the nitrifying bacteria are weak compared with those of heterotrophic bacteria.

For waters with a very small organic load such as underground water sources it is recommended to use an inert filter media such as expanded clay granules. This types of water tend to form a so-called *pure nitrification culture* [11] with a minimized heterotrophic component when aerated. The expanded clay granules, which can be characterized as having a porous surface and a high specific surface area can equip an upflow biological aerated filter (in order to avoid short circuiting and clogging) and can favor the fixation and maintaining the biomass attached.

Because of multiple factors that can influence the process [12], related to 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, morphology, surface area) and the type and operation parameters of the bioreactor (dissolved oxygen concentration, filtration rate, empty biological contact time, washing parameters) nitrification performances reported in literature enroll in a wide range of values [13], difficult to use for a particular case, without a case study. The nitrification performance reported to the filter height, reflected by concentration fronts in the biofilter, is important for the BAF design and configuration.

A pilot scale BAF with expanded clay media was used in this study in order to determine the ammonium removal rate from an underground water source and to determine the concentration fronts depending on the height of the filter media (at low reaction temperature and by using a low cost filtration media).

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Experimental part

Materials and methods

Given Romania's current situation, where the nitrification process does not apply as a pretreatment stage in drinking water treatment, the nitrification experiment had the following goals:

- to determine the nitrification performance achievable in the context of a certain groundwater composition matrix, using an upflow biological aerated filter (having a low-cost assortment of expanded clay granules as a filter media) at relatively low reaction temperatures;
- to determine the evolution of inorganic forms of nitrogen concentration fronts involved in the nitrification process vs. the height of the filter media.

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

- analytical investigation of the underground water source in order to determine the variation domains of the main parameters of interest in a biological nitrification process: *p*H, NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}, alkalinity, Fe, Mn, organic matter;
- countinous pilot scale biological aerated filter design and bilt;
- inoculation of the inert granular filter media;
- bioreactor operation, in usual areas of operating parameters, with N-NH_4^+ loadings within the maximum nitrification capacity limit and even higher;
- influent and effluent (sampled from different heights of the filter media) analytical investigation in order to determine NH_4^+, NO_2^-, NO_3^- concentrations;
- ammonium removal rate evaluation.

The biological nitrification experiment was conducted in a continuous pilot scale biological aerated filte operated in upflow mode (fig. 1). The influent used was the same as the one from a drinking water treatment plant, near Bucharest, Romania. The biofilter with a diameter of 0.125 m was filled with expanded clay granules to a height of 1.20 m.

The expanded clay granules used as a filter media represented the 2-5mm granulometrical fraction of Laterlite™ Leca commercial assortment, obtained by sieving. The filter media characteristics are shown in table 1. The expanded clay granules surface morphology is shown in figure 2, which represents a SEM micrograph (1000x).

After a two months period dedicated to the inoculation of the expanded clay media, the nitrification experiments

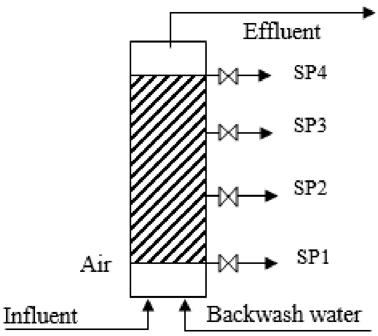

Fig. 1. Schematic of up-flow BAF

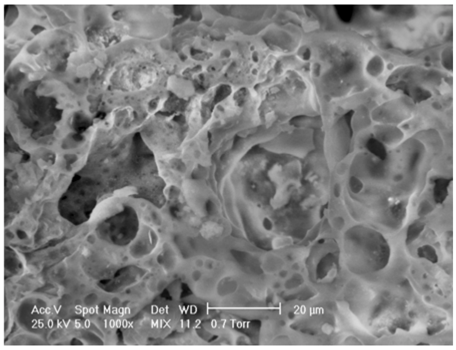

Fig. 2 Scanning electron micrograph of a Leca Laterlite™ granule

were conducted within 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 35 m/h and 60 m/h. The nitrification process evolution in the bioreactor was investigated by analytical methods that determined the ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-) concentrations in the influent and effluents (sampled from different heights of the filtering layer). The inorganic nitrogen forms concentrations, previously mentioned, as well as the concentration of the phosphate ion (PO_4^{3-}), were determined by ion chromatography using 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 of interest for the process were investigated as follows: the 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 influent analytical investigations revealed the concentration range of main quality parameters of interest for the studied biological process (table 3), highlighting the high concentration of ammonium ions (2.75 - 6.15 mg/L), far above the maximum admissible limit (0.5 mg/L).

Nitrification performance

Ammonium removal rate was calculated according to the following equation:

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

where:

r_v - ammonium removal rate, g NH_4^+-N/day * m^3 media;
Q_{in} - influent flowrate, m^3/day;
S_{in} - influent NH_4^+ - N concentration, mg/L;
S_{ef} - pseudo steady state effluent NH_4^+ - N concentration and NO_2^- - N concentration sum for each loading condition, mg/L;
V_b - volume of filter media, m^3.

Table 1
CHARACTERISTICS OF LECA LATERLITE™ MEDIA

Media size, [mm]	Effective size, [mm]	Density, [kg/m³]	Bulk density, [kg/m³]	Porosity, [%]	BET surface area, [m²/g]
2-5	2.3	815	440	46	0.71

Table 2
OPERATING PARAMETERS FOR BAF

Average temp. in BAF, [° C]	Dissolved oxygen in effluent, [mg/L]	Empty bed contact time, [min.]	Filtration rate, [m/h]
10.2 - 13.5	4.1 – 7.5	4.3 -7.4	4.45 - 7.63

Parameter	Measure unit	Range	Permitted value by Romanian Law 458/2002, republished in 2011
pH	-	7.84 – 8.49	6.5 – 9.5
Alcalinity	mg HCO_3^-/L	277 – 341	-
NH_4^+	mg/L	2.75 – 6.15	0.5
NO_3^-	mg/L	< 0.1	50
NO_2^-	mg/L	< 0.1	0.1
PO_4^{3-}	mg/L	0.63 – 1.56	-
Mn	µg/L	≤50	50
Fe	µg/L	≤200	200
TOC	mg/L	3.1 – 3.5	No significant modifications

Table 3
GROUNDWATER CHARACTERISTICS

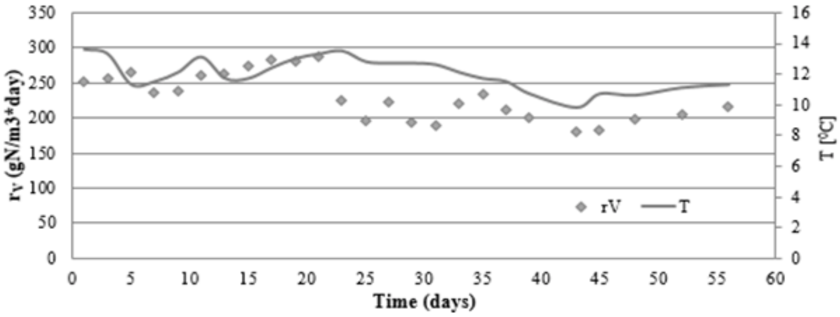

Fig. 3. Ammonium removal rate versus reaction temperature for BAF with 2-5 mm expanded clay media

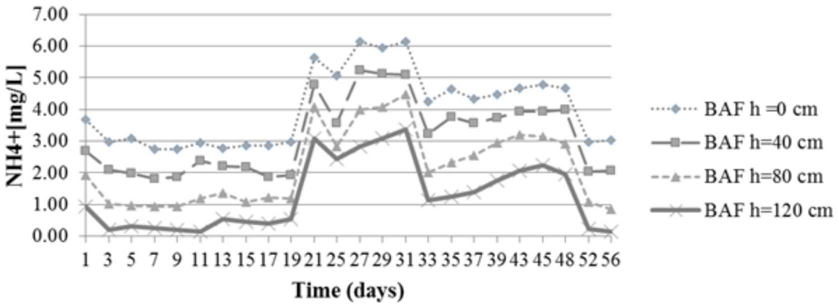

Fig. 4. NH_4^+ concentration front evolution in BAF

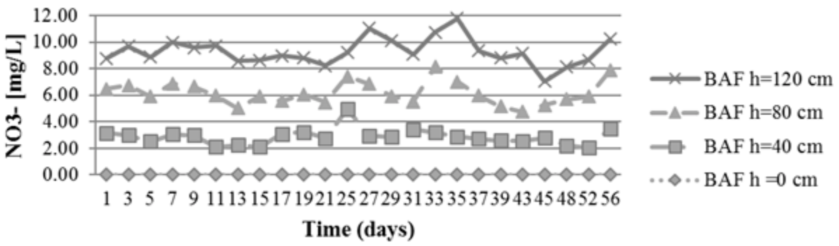

Fig. 5. NO_3^- concentration front evolution in BAF

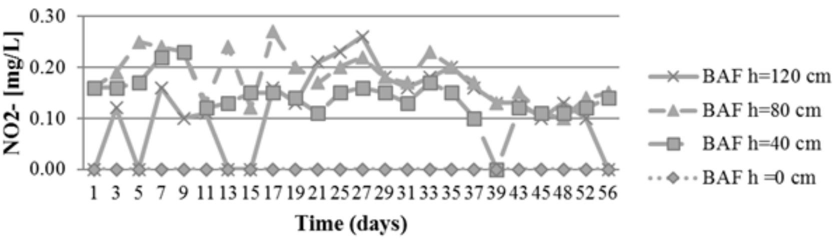

Fig. 6. NO_2^- concentration front evolution in BAF

Given the relatively low reaction temperature (10.2 - 13.5ºC) and by using low cost expanded clay granules (2-5 mm) as a filter media, the ammonium removal rate varied between 180 – 288 g NH_4^+-N/day * m^3 media (fig. 3). By comparison, the ammonium removal rates reported in literature [14] varied between 0.25 - 0.6 kg NH_4^+-N / day * m^3 media, depending on the reaction temperature and the type and effective size of the filter media.

Concentration fronts evolution in BAF

Influent and effluent samplings from the bioreactor at different heights (0 m, 40 cm, 80 cm and 120 cm), that divided the filter media into three equal parts, and the analytical determination of the inorganic forms of nitrogen concentrations where used to asses ammonium (NH_4^+), nitrate (NO_3^-) and nitrite (NO_2^-) concentration fronts (figs. 4, 5 and 6).

The graphs in figure 4 and 5 indicate that the nitrification process occurred relatively homogenously within all three equal segments of the filter media, given the facts that the process was operated without dissolved oxygen limitations and with ammonium influent loads at the nitrification capacity (and above) of the bioreactor. The concentration fronts distribution by height of the biofilter are primarily determined by the ammonium influent load and nitrification capacity of the BAF (figs. 4, 5).

During the initial testing period (day 3 - day 19) when the ammonium influent loads did not exceed the BAF nitrification capacity, NH_4^+ and NO_3^- concentration, were below the maximum admissible limits and NO_2^- concentration was situated close to the maximum limit impose.

During the experimentation period, when the ammonium influent load applied exceeded, sometimes substantially, the BAF nitrification capacity, NH_4^+, NO_3^- and NO_2^- concentrations in the final effluent exceeded the imposed limits.

Conclusions

The analytical characterization of groundwater used as drinking water source, both in the treatment plant and in the pilot scale BAF system, emphasized the fact that the ammonium concentrations were much higher than the concentration limit imposed.

It has been experimentally demonstrated, that the ammonium ion removal from groundwater (intended for human consumption) can be achieved by nitrification, method unused so far in Romanian treatment plants, thus avoiding the breakpoint chlorination disadvantages (reagents costs, reagents introduction in drinking water, the occurrence of undesirable reaction byproducts).

The nitrification performance, reflected in the ammonium removal rates obtained experimentally in low temperature conditions and using a low cost, non-specialized filter media, are in the value range reported by literature.

By using a low cost filter media it is possible to reduce investment and maintenance costs of a biological treatment step of raw water with high ammonium concentration, intended for human consumption.

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