U.P.B. Sci. Bull., Series B, Vol. 77, Iss. 4, 2015 ISSN 1454-2331

INFLUENCE OF BIOLOGICAL FILTRATION MEDIA ON THE AMMONIUM REMOVAL RATES FROM GROUNDWATER SOURCES

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The paper investigates the influence of the filter media (Leca, Kaldnes) and hydrodynamic configuration (Kaldnes, aeration within the filter media; Kaldnes, pre-aeration of influent and effluent recycle) on the removal performances of ammonium nitrogen (NH_4^+ -N) from groundwater sources in biological aerated filters. The results showed that the volumetric removal rates of NH_4^+ -N were higher for the Leca media (97-261 kg N/m^3/day) than for Kaldnes media (30-135 kg N/m^3/day), and also for the biofilter with pre-aeration (30-135 kg N/m^3/day) than for the aeration within the filter media (13-66 kg N/m^3/ day).

Keywords: groundwater, ammonium nitrogen, biological aerated filter, filter media, hydrodynamic configuration

1. Introduction

The main sources for ammonium nitrogen discharges into soil and groundwater are represented by fertilizers' industry, sewerages, agricultural activities and leachates from waste dumps that are affecting raw water resources. Their impact is materialized in specific ways like: eutrophication, low dissolved oxygen, toxicity on aquatic environment [1], [2].

Ammonium removal from water sources is usually performed by physical and chemical methods, the most common being the "breakpoint" chlorination.

The presence of ammonium nitrogen in high concentrations in raw water, above the imposed concentration limit of 0.5 mg/L, value accepted by European Union [3], can lead to compromised chlorination process, due to the fact that ammonium reacts with the chlorine, resulting in an insufficient chlorine

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disinfection within the distribution network [4], odor, taste and public health issues generated by chloramines, which are carcinogenic by-products [5].

In wastewater treatment, the biological methods are routinely applied for ammonium removal by classic (conventional) nitrification [6] or by recently developed processes of Sharon / Anammox [7]. Even if the biological processes are less applied for drinking water treatment, the attention for these methods has significantly increased in the last years, due to the several advantages: no use of chemicals and decrease of sludge volume which allow its easier handling.

Nitrification intermediated by autotrophic bacteria is the most common biological process used for ammonium removal from water sources. The process involves two-step oxidation, that implies two groups of bacteria: (1) *Nitroso*-bacteria, such as *Nitrosomonas sp.*, which oxidize ammonium nitrogen to nitrite (AOB) and (2) *Nitro*-bacteria, such as *Nitrobacter sp.*, which further oxidize the nitrite to nitrate (NOB), in both reactions oxygen being the electron acceptor [6]:

$$NH_4 + 1.5\,O_2 \rightarrow NO_2 + H_2O + 2H \quad (1)$$

$$NO_2 + 0.5O_2 \rightarrow NO_3 \quad (2)$$

Biological oxidation of ammonium can be performed using Biological Aerated Filters (BAFs). The BAF system was initially used about four decades ago, being proposed as a promising alternative for wastewater treatment [8]. Compared to other fixed-film systems (e.g. trickling filters), BAF system has several important advantages, such as: compactness, high biomass content, high solids retention time, higher resistance for shock-pressure, dual function of filtering for organic and inorganic pollutants removal, simple maintenance and operation. There are also several drawbacks related to BAF using, such as: the risk of filter clogging and the costs associated for system's aeration and washing [9]. In order to meet regulatory requirements and taking into consideration the economic factor, nowadays it is very important to provide an efficient, environmentally friendly bio-filtration system with low cost investment.

The performances of bio-filtration processes are dependent mainly on the following factors: temperature, oxygen supply, nutrients supply, process operation (e. g. retention time, backwashing, upflow/downflow configuration), filter media properties (specific area, size), etc. [10], [11], [12].

The filter media type represents a critical factor in the process operation and system's design, and has direct influence on the treatment performances governing the economic and environmental viability of the BAF system [13]. Several media types (e.g. zeolite, expanded/burned clay, ceramic, glass, plastic, etc.) were tested for secondary/tertiary wastewater treatment, many lab scale experiments involved the use of synthetic medium. Moreover, various types of filter media were selected, depending on the application type envisaged.

The influence of the media type and hydrodynamic operating conditions on real groundwater treatment performances (pure nitrification, in this case) achieved in terms of volumetric NH_4^+ removal rate using pilot-scaled BAF systems packed with Leca (light expanded clay aggregate) and Kaldnes media were investigated.

Analytical monitoring of ionic species involved in biological oxidation reactions of ammonium in water can be achieved by ion chromatography [14].

2. Materials and methods

2.1. On- line lab-scale BAF systems

The experiment was performed in three BAF's equipped with two types of media (Kaldnes; Leca) and operated in different hydrodynamic configuration (up-flow / down flow; aeration within the filter media / pre-aeration), as presented in Table 1.

Table 1

Experimental operating conditions and parameters for biological aerated filters

Media type and hydrodynamic configuration of BAF	Effluent temp., [^{o}C]	Dissolved oxygen, [mg/L]	Empty bed contact time, [min.]	Filtration rate, [m/h]
Kaldnes; up-flow; aeration in media bed	11- 19.3	6.3- 7.9	29- 79	1.27- 3.44
Kaldnes; up-flow; pre-aeration of influent and recirculated effluent	11.6- 18.8	2.9- 5.7	13- 72	1.43- 2.82
Leca; down-flow; aeration in media bed	15.4- 18	2.5- 6.7	4- 20	1.37- 6.36

Variation ranges of some important operational parameters are also presented in this table, such as: effluent temperature, dissolved oxygen concentration, filtration rate and water- biofilm contact time calculated as empty bed contact time (EBCT). For the development of nitrifying biofilm, three BAF's were equipped with two kinds of filter media with specific characteristics, as described in Table 2:

Table 2

Characteristics of filter media

Material	Media size (mm)	Density (kg/m^3)	Bulk density (kg/m^3)	Porosity (%)	Specific/BET surface area
Kaldnes	diam. x height = 16 x 9	750	250	67	750 m^2/m^3
Leca	4-10, granular; effective size = 4.6	770	385	50	0.71 m^2/g

- Kaldnes- cylindrical plastic geometric solids with smooth surfaces;
- Leca- expanded clay granular material.

All BAF's in the experiment worked in parallel, being fed with the same groundwater as influent.

2.3. Raw water characteristics

The influent for the on-line lab-scale BAF's was represented by a source of raw groundwater from Bragadiru, Romania, with the following characteristics (*Table 3):*

Table 3

Groundwater characteristics

Parameter	Measure unit	Range	Permitted value by Romanian Law 458(r1)/2002 republished in 2011
pH	-	7.73 - 8.84	6.5 – 9.5
Alcalinity	mg HCO_3^-/L	277 – 341	-
PO_4^{3-}	mg/L	0.65 – 1.53	-
NH_4^+	mg/L	2.91 – 5.21	0.5
NO_3^-	mg/L	< 0.1 – 0.21	50
NO_2^-	mg/L	< 0.1	0.1

2.4. Analytical methods

During the experimental period, influent and effluent samples were sampled regularly and analyzed for ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-) and phosphate (PO_4^{3-}) concentration. The analysis were performed by ion chromatography, using ICS-3000 system (Dionex, USA) according to the standardized methotd: SR EN ISO 14911:2003 (in case of NH_4^+) and SR EN ISO 10304/1:2009 (for anions). Another parameter investigated was the inorganic carbon content determined as bicarbonate (HCO_3^-), according to the SR ISO 9963/1/A99:2002 standard. Variation of operational parameters was also monitored for pH, temperature (Model C932, Consort, Belgium) and dissolved oxygen concentration (DO) (Model Oxi320, WTW, Germany).

3. Results and discussion

The nitrification performance in all three experimental biological aerated filters, expressed as the volumetric ammonium removal rate, was calculated according to the following equation:

$$r_V = \frac{Q_{in}(S_{in} - S_{ef})}{V_b} \tag{3}$$

where:

r_V - volumetric NH_4^+ removal rate, g NH_4^+- N/m^3 packed media/day;
Q_{in} - volumetric flowrate of influent, m^3/day;
S_{in} - influent NH_4^+ -N concentration, mg/L;
S_{ef} - pseudo steady state effluent NH_4^+ - N concentration at each loading condition, mg/L;
V_b - volume of packed media, m^3.

3.1. The bioreactor filled with Kaldnes media, operated in upflow mode and aeration within the filter media

The nitrification rates were situated in the range of 13-66 g NH_4^+ - N/m^3/day (Fig. 1). These rates were obtained at reaction temperatures situated in the range of 11 to 19.3 ° C, and for an empty bed contact time (EBCT) of 29 to 79 minutes. These relative low performances could be explained by the fact that the smooth surfaces of the filter media does not facilitate bacterial adhesion and biofilm development, while the aeration within the packed media favors biomass detachment and washout.

The residual NH_4^+ concentrations in the effluent were, with some exceptions, above the maximum allowed limit of 0.5 mg /L, revealing that the loading rates exceeded the nitrification capacity of the biofilter.

The biofilter did not require washing, due to high void fraction (67%) and their large size.

3.2. The bioreactor filled with Kaldnes media, operated in upflow mode, with influent and recirculated effluent pre-aeration

The nitrification rates obtained in this bioreactor ranged between 30 and 135 g NH_4^+- N/m^3/day (Fig. 2).

Except for the first period (days 4 to 20), which corresponded to the biological start-up, the nitrification rates obtained in the following period (days 20 to 79) were situated in the range of 59- 135 g N-NH_4^+ oxidized/m^3/ day, for empty bed contact times of 13 to 49 minutes, filtration rates in the range of 1.57 - 2.82 m/h and normal reaction temperatures (14,6 to 18.8 ^{o}C). The nitrification rates were relatively low, but, anyway, almost double than those obtained in the bioreactor filled with Kaldnes media operated in upflow mode with aeration in the packed media (Fig. 4) The explanation resides in the fact that the smooth surfaces of the filter media does not facilitate bacteria adhesion and biofilm development. However, by changing the aeration strategy, with the price of effluent recirculation to ensure the required oxygen favored the biochemical reactions, we avoided the aeration within the packed media..

3.3. The bioreactor filled with Leca media, operated in downflow mode and with aeration within the packed media

The nitrification rates obtained in the bioreactor filled with Leca media, operated downflow and with aeration within the filter medium ranged between 97 and 261 g NH_4^+ - N/m^3/day (Fig. 3).

During the initial period (days 47-54), nitrification was complete, the residual concentrations of NH_4^+ and NO_2^- are below the limits of 0.5 mg/l and 0.1 mg/l respectively, a sign that the bioreactor was operated with N-NH_4^+ loadings below the possible maximum nitrification capacity.

In the next period (days 57 to 79), the ammonium loads were increased in order to identify the range of maximum nitrification rates attainable in the specific conditions of this bioreactor. The nitrification rates obtained ranged between 163 and 261 g NH_4^+ - N oxidized/ m^3/day, for empty bed contact times ranging from 4.2 to 7.2 minutes, filtration rates in the range of 3.52 to 6.46 m/h and reaction temperatures of 15,4 to 17.9 ^oC. The nitrification rates were higher (approximately two times) than those obtained in the bioreactor filled with Kaldnes media operated in upflow mode and with pre-aeration of influent and recirculated effluent (Figure 4). The explanation resides in the fact that the porous surface of the granular media facilitated the adhesion of bacteria and biofilm development.

Residual concentrations of NH_4^+ in the effluent were, with some exceptions, higher than the maximum allowed limit of 0.5 mg/l, revealing that the bioreactor was operated with ammonium loads that exceeded the nitrification capacity of the biofilter.

Once the level of water in the biofilter increased with 0.5 m, the biofilter was washed according to the following sequence of operations:

- Loosening with air for 5 minutes, at a filtration rate of 40-50 m/h;
- Washing for 5 minutes with water and air by co-current application of water and air at about 20-25 m/h and 40-50 m/h, respectively;
- Rinsing with water for 10 minutes, at a filtration rate of 20-25 m/h.

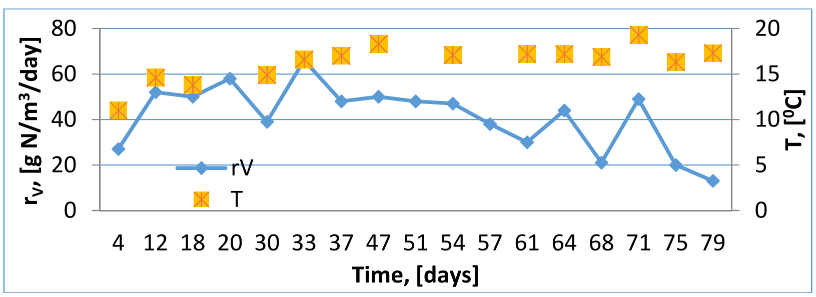

Fig. 1. Volumetric ammonium removal rates obtained in BAF with Kaldnes media, operated in upflow mode and with aeration within the packed media

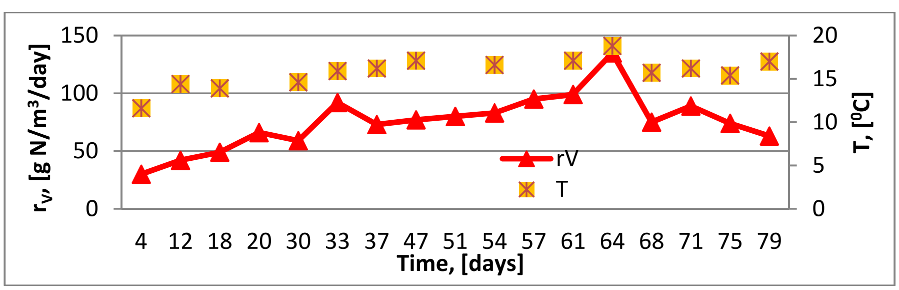

Fig. 2. Volumetric ammonium removal rates obtained in BAF with Kaldnes media, operated in upflow mode and with pre-aeration of the influent and recirculated effluent

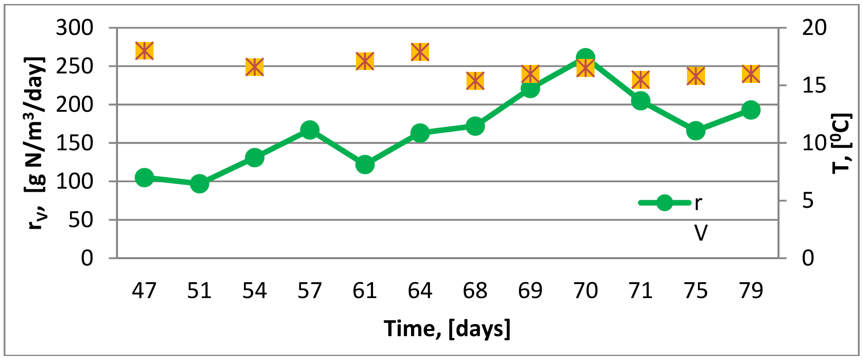

Fig. 3. Volumetric ammonium removal rates obtained in BAF with Leca media, operated in downflow mode and with aeration within the packed media

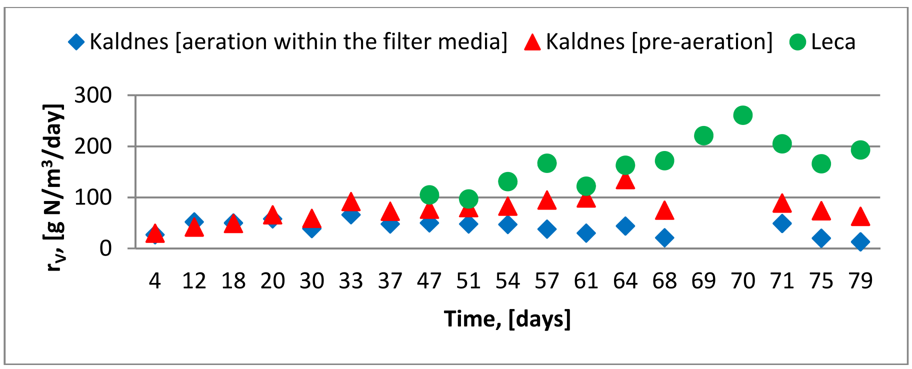

Fig. 4. Comparative representation of the volumetric ammonium removal rates in all BAF's with different filling media and different hydrodynamic configurations.

4. Conclusions

The nitrification experiment for groundwater source (the so-called pure nitrification) led to the following conclusions:

• granular media - Leca type, having a low price, is a suitable medium for nitrifying biofilm development, due to rough surfaces with pores, which allow the adhesion of nitrifying bacteria;

• granular media - Leca type is more suitable for pure nitrification than plastic media - Kaldnes type with smooth surfaces, due to higher specific surface and the advantage conferred by the porous surfaces, in comparison with smooth surfaces in fixing and biofilm development;

• nitrifying bacteria adhesion and biofilm development on smooth surfaces (as in Kaldnes media) is sensitive to the hydrodynamic regime of the reactor, turbulences (as, for example, those created by aeration in the packed media) favoring biofilm detachment and washout, with a negative impact on the nitrification rates.

Acknowledgements

The work was supported by Project SOP HRD - PERFORM /159/1.5/S/138963 and Programme Nucleu 13N/2009, Project PN 09 - 13 03 03.

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