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WATER DENITRIFICATION BY DISPLACEMENT BIOFILTRATION

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This work was aimed creating a simple and reliable submersed biofilter for the decentralized treatment of nitrate-contaminated water. Denitrification of water was studied by the method of displacement (piston) bio-filtration in specially designed devices intended for home application. At certain sizes of grains of bio-filtration bed and filtration flow directions in it, the change in operating mode of denitrifying biofilter from direct flow to displacement mode offers the following advantages. There is no need to maintain a continuous and slow flow of water through the biofilter. The consumers have the opportunity to feed big portions of water into the bio-filter in one gulp (pulse) and nevertheless get the same quantity of denitrified water. The design of created biofilters is simple. Assembling these bio-filters implies the use of materials with a minimum carbon footprint.

Keywords: biofiltration, displacement mode, drinking water, removal of nitrates, water purification.

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Introduction

Last decades, the mineral composition of groundwater has deteriorated in the settlements of agricultural territories and the suburbs of large cities. There, the water from wells and boreholes exhibit a nitrate concentration significantly exceeding sanitary and hygienic limits. An excessive concentration of nitrates in drinking water causes methemoglobinemia in infants and provokes malignant tumors and other dangerous diseases in adults [1].

Contamination of groundwater with nitrates is due to the use of nitrogen fertilizers in crop production, the disposal of insufficiently treated wastewater into surface streams out of livestock (poultry) farms and sewage water from the households. As a result, the concentration of nitrates in groundwater exceeds the maximum permissible concentration (45 mg dm^{-3}) in vast territories of many countries [2].

Causal relationships in the pollution of water sources with nitrates were investigated in the middle of the last century in Germany. Since that, the problem of drinking water purification from nitrates is dealt with specialists ensuring the safety of centralized water supply and those who solve the problems of decentralized water treatment.

Currently [3], the ion exchange filtration, adsorption filtration, electrochemical reduction and electrodialysis, reverse osmosis, and microbiological reduction of nitrates to molecular nitrogen in filtering devices with mobile and fixed carriers of attached microflora are used to remove nitrates from drinking water. Each of the listed methods ensures the fulfillment of the task, but the first four of them are not environmentally friendly and optimal from their life cycles (carbon footprint). The last one, biofiltration, is used within the centralized treatment of water, but not in the devices of the point of use (decentralized water treatment).

This is due to the specifics of biofiltration reduction of nitrates to nitrogen gas by heterotrophic and autotrophic bacteria. Under favorable conditions in apparatuses with a submersed fixed filtration bed, denitrifying bacteria form powerful biofoulings over time. Their biomass accumulates especially rapidly when processing water with a high nitrate concentration. As a result, the clogging occurs in biofilter when the grains of the filtration bed are of small size. To carry out biofiltration under these conditions, special dispensers, pumps and flushing devices are required. When a fluidized carrier is used as a support of the attached microflora, the biofilter must also have reliable tools to ensure the effective circulation of that carrier and removal of accumulating plankton. Denitrifying autotrophs do not form powerful biofoulings, but raise the problem

of cumbersome filtering devices since the nitrate bioremediation rate by autotrophic bacteria is low.

The biochemical mechanisms and technological features of microbiological denitrification at the row water and wastewater treatment have been intensively studied over the past decades. The denitrification under the action of heterotrophic and autotrophic microorganisms and the basic chemical equations of biodenitrification were described elsewhere [2,4,5], the requirements of carbon sources (electron donors) for denitrification bacteria were also indicated there. Removal of nitrates from water utilizing denitrifying heterotrophic microorganisms can be attained at appropriate feeding of easily digestible hydrocarbons as donors of electrons. Any non-toxic granular filtering bed or other filtration material is able to fix and multiply denitrifying bacteria. Autotrophic denitrification occurs under strictly anaerobic conditions in the presence of inorganic electron donors (hydrogen, sulfur, etc.) and sources of inorganic carbon. Denitrifying of water under the action of autotrophic bacteria was studied in ref. [6]. A feature of autotrophic denitrification is that its run does not require sources of organic carbon. However, the slow rates of constructive and energy metabolism in autotrophic bacteria hinder the creation of the biofilters of home-used with the participation of these microbes.

This work was aimed at creating a simple and reliable submersed biofilter for the decentralized treatment of nitrate-contaminated water. We assumed that at certain grain sizes of filtration bed a special design of the biofiltration device allows changing the operating mode of a denitrifying biofilter from a continuous flow to a periodical displacement biofiltration.

The usage of discrete pulses of supplied water as opposed to continuous injections allows reducing the filter clogging and channeling. As a result, the required degree of water denitrification can be achieved on a stably functioning biofilter without the use of special injecting and flushing devices.

Theory

At the ratio of height to diameter greater than 20, the submersed biofilters with a fixed filtration bed can be considered as reactors of ideal displacement. In these reactors, the stirring is absent along the filtration axis and the uniform distribution of the concentration of substances occurs in the direction perpendicular to this axis. The mathematical model of the biofilter as an ideal displacement reactor can be written by the following equation:

$$\frac{\partial C_i}{\partial \tau} = -u\frac{\partial C_i}{\partial l}, \quad (1)$$

where C_i is the concentration of the i-th substance inside the biofilter, τ is the time, u is the linear filtration rate, and l is the coordinate along the axis (the length of filtration path).

The differential equation (1) describes the variation of substance concentrations inside the flow of water vs. time and filtration rate. If one uses in Eq. (1) the volumetric flow rate υ instead of the linear filtration rate (u) ($u=\upsilon/S$), then we get:

$$S\frac{\partial C_i}{\partial \tau} = -\upsilon\frac{\partial C_i}{\partial l}, \quad (2)$$

where S is the cross-section of the filtration bed.

Taking into account in Eqs. (1) and (2) the source of changing the concentrations of substances due to chemical or biochemical reactions (W_i), one can obtain the following equations of material balance:

$$\frac{\partial C_i}{\partial \tau} = -u\frac{\partial C_i}{\partial l} \pm W_i, \quad (3)$$

$$S\frac{\partial C_i}{\partial \tau} = -\upsilon\frac{\partial C_i}{\partial l} \pm W_i, \quad (4)$$

where C_i is the concentration of the i-th substance in the filtration flow, and W_i is the rate of a chemical or biochemical reaction concerning the i-th substance.

The microbiological denitrification is the multi-stage reaction:

$$2NO_3^- \rightarrow 2NO_2^- \rightarrow 2NO \rightarrow N_2O \rightarrow N_2. \quad (5)$$

This reaction is provided by the action of coordinated enzymes in bacterial cells [7].

The process of microbiological denitrification can be simulated by multiple Monod kinetics model. This model focuses on the application of the Monod equation for both electron donors and electron acceptors coupled with biomass growth as described elsewhere [8]:

$$W_{ED} = -k_{max}\frac{[ED]}{[ED]+K_{S\,ED}}\frac{[EA]}{[EA]+K_{S\,EA}}[X], \quad (6)$$

$$W_{EA} = QW_{ED}, \quad (7)$$

$$W_X = -Y_h W_{ED} - b[X], \quad (8)$$

where W_{ED} is the rate of change in the concentration

[M L^{-3} τ^{-1}] of electron donor, [ED] is the concentration [M L^{-3}] of the electron donor, W_{EA} is the rate of change in the concentration [M L^{-3} τ^{-1}] of the electron acceptor, [EA] is the concentration [M L^{-3}] of electron acceptor, W_X is the rate of change in the concentration [M L^{-3} τ^{-1}] of biomass, [X] is the biomass concentration [M L^{-3}], Y_h is the microbial yield, Q is the stoichiometric parameter, k_{max} is the maximum consumption rate [τ^{-1}] of electron donor, b is the kinetics parameter for biomass yield accounting for endogenous decay, and $K_{S\ ED}$ and $K_{S\ EA}$ are respective electron donor and electron acceptor concentrations at which the biomass growth rate is half its potential maximum value.

To analyze in detail the denitrification process inside of biofilter, one should integrate Eq. (3) or (4) in consideration of Eqs. (6)–(8). In general, the biodegradation kinetics is determined by the life stage of biomass (lag phase, exponential growth, stationary phase or decay) and nutrient availability. When biomass grows exponentially, the substrate concentration is much lower than the saturation constant, and Monod kinetics transforms to the first-order kind with respect to the substrate. When biomass is in the stationary phase and there no nutrient limitations, the Monod kinetics transforms to the zero-order one, because the substrate concentration is much higher in this state than the saturation constant [9]. If the rate of the process is limited by the concentration of both biomass and substrate, the kinetics obeys the second order equation. Since the denitrification bacteria perform their functions on the surface and inside the matter of biofilms, the rate of the process depends upon the quantity of biomass and substrate concentration. To carry out a primary analysis, one can consider the rate of the reduction of nitrate concentration as a reaction of order «n» using the following expression:

$$W_{NO_3^-} = k\left(C_{NO_3^-}\right)^n, \qquad (9)$$

where k is the constant of biofiltration rate with respect to nitrate ions, and n is the order of the reaction.

It is important to note that «n» is subjected to changes with changing the conditions of biofiltration. The variation of biofiltration conditions initiates the redistribution of biomass and substrates concentrations along the biofiltration pathway. As a result, at different ages (states) of biofilms on the grains of filtration bed and different schemes of substrates loads to biofilter, the order of reaction of nitrates transforming into nitrogen gas will be different. In such a way, the experimental dynamics of biofiltration is reasonable to analyze using the following equation:

$$\frac{\partial C_{NO_3^-}}{\partial \tau} = -u\frac{\partial C_{NO_3^-}}{\partial l} - k\left(C_{NO_3^-}\right)^n. \qquad (10)$$

For a steady-state biofiltration mode with a constant flow rate (u) of the water through the biofilter, the following equations will be valid:

$$\frac{\partial C_{NO_3^-}}{\partial \tau} = 0, \qquad (11)$$

$$\text{and} \quad u\frac{\partial C_{NO_3^-}}{\partial l} = -k\left(C_{NO_3^-}\right)^n \qquad (12)$$

$$\text{or} \quad \frac{dC_{NO_3^-}}{\left(C_{NO_3^-}\right)^n} = -\frac{k}{u}dl. \qquad (13)$$

Inserting the values of n=0, n=1 and n=2 (zero, first and second orders of the reaction of nitrates reduction, respectively) into Eq. (13) and integrating it within the limits from $C_{in\ NO_3^-}$ to $C_{out\ NO_3^-}$ (for C) and from zero to l (for l), one gets:

$$C_{out\ NO_3^-} = C_{in\ NO_3^-} - k_0\frac{l}{u}; \qquad (14)$$

$$C_{out\ NO_3^-} = C_{in\ NO_3^-}\exp\left(-k_1\frac{l}{u}\right); \qquad (15)$$

$$C_{out\ NO_3^-} = \frac{1}{k_2\dfrac{l}{u} + \dfrac{1}{C_{in\ NO_3^-}}}. \qquad (16)$$

If instead of steady-state flow, the non-flowing mode of water denitrification is used (u=0), then we have:

$$u\frac{\partial C_{NO_3^-}}{\partial l} = 0 \qquad (17)$$

$$\text{and} \quad \frac{dC_{NO_3^-}}{dl} = -k\left(C_{NO_3^-}\right)^n \qquad (18)$$

or $$\frac{dC_{NO_3^-}}{\left(C_{NO_3^-}\right)^n} = -kdt. \quad (19)$$

Integration of Eq. (19) at n=0, n=1 and n=2 within the limits from $C_{(\tau=0)NO_3^-}$ to $C_{(\tau)NO_3^-}$ (for concentration) and from zero to τ (for time) yields the following expressions:

$$C_{(\tau)NO_3^-} = C_{(\tau=0)NO_3^-} - k_0\tau; \quad (20)$$

$$C_{(\tau)NO_3^-} = C_{(\tau=0)NO_3^-} \cdot \exp\left(-k_1\tau\right); \quad (21)$$

$$C_{(\tau)NO_3^-} = \frac{1}{k_2\tau + \frac{1}{C_{(\tau=0)NO_3^-}}}. \quad (22)$$

Comparing Eqs. (14)–(16) and (20)–(22), one can see that the concentrations of NO_3^- will be equal to each other at the exit of biofilter at both modes of biofiltration if the retention time of these ions inside the biofilters is the same at the direct flow (the magnitude l/u) and zero flow (the magnitude τ). In other words, if the water contaminated with nitrates enters into the biofilter as discrete portions (discrete pulses) through time intervals τ=l/u, then the equal portions of denitrified water will come out with the same concentration that at continuous flow mode when u=l/τ. The completeness of denitrification will depend on the initial concentration of nitrates in water under treatment and nutrients concentration in it, the kind of used denitrifying microflora and its activity along the biofiltration pathway, the volume of the portions of water supplied to the biofilter, and how often it does. The last factor affects the hydraulic retention time. The structure of the filtration bed (the surface area available for biofouling, pore space configuration, the thickness of arisen biofouling and its age) is a crucial factor too.

Experimental

The nitrates removal was carried out by the method of displacement biofiltration in specially designed U-shaped biofiltering devices. These devices were assembled using standard polyvinyl chloride pipes with an inner diameter of 100 mm and a height of 1500 mm, a blanked bottom and a hydraulic jumper with an outlet valve installed at a distance of 50 mm from the blanked bottom. In the upper part of each of the pipes forming a U-shaped construction, the holes were made apart of 200 mm from their open upper ends, and suitable tubing was mounted to supply water for filtration and drain filtered water. Thus, water moved in a top-down direction and in a bottom-up one in the inlet knee of the biofilter and in the outlet knee, respectively. It was also possible to take water samples for analysis from the bottom of the biofilter.

To carry out heterotrophic denitrification, the HDPE filter media consisting of profiled hollow polyethylene rollers was used. The size of the rollers was 16×12 mm, the surface area was 1000 $m^2\ m^{-3}$ and the specific free space was 0.75 m^3 per cubic meter of bulk material.

To carry out autotrophic denitrification, the U-shaped case was filled with a mixture of granular sulfur and marble chips in the ratio of 1:1.5 as described elsewhere [6]. Autotrophic microflora has an appropriate niche on the grains of this filtration bed. The diameter of the sulfur granules and the size of grains of marble chips were in the range of 6–8 mm. The specific free space in this filtration bed was approximately 0.42 m^3 per cubic meter of material used. In each of the biofilter elbows, the filtration path was equal to 1200 mm. The volume of water filling the HDPE filter media was 15 dm^3, and the volume of water filling the bed of sulfur and marble granules was about 10 dm^3. The seeding matter and the aquatic environment for incubating denitrifying biofoulings inside of each bed was water taken from the Dnieper River (Ukraine, Dnipro, Monastery district) at a depth of 0.5 m. Sodium nitrate and ethyl alcohol were added to this water sample to ensure the incubation of biofouling of denitrifying heterotrophs on rollers of HDPE. The dosage of ethanol was 0.8 mg per 1 mg of treated nitrates $\left(NO_3^-\right)$ as used in work [10]. Initial nitrate and alcohol concentration in incubation water was 595 mg L^{-1} (7 mM $NaNO_3$) and 347 mg L^{-1} of absolute ethyl alcohol. To create appropriate conditions for the attachment and growth of autotrophic denitrification bacteria on sulfur and marble granules, only sodium nitrate (7 mM $NaNO_3$) was added to incubation water.

The incubation of denitrifying biofoulings was similar in the main on the grains of both filtration beds. Each download was placed into a polycarbonate container (35 cm in height and 26 cm in diameter), filled with incubation water (river water and additives mentioned above), and kept at a temperature of 18–25°C for three months. During that time, a slow pumping of the incubation water through the pore space of filter beds was conducted in the direction from the top to the bottom in the closed-loop system. The pumping rate was equal to $2.3 \cdot 10^{-2}$ $cm^3\ s^{-1}$

(i.e. ~2 liters per day). The concentration of nitrate ions and pH in the circulating water was measured within the incubation. After three months of the incubation period, the color of the filtration bed gradually changed from white (initial color of polypropylene) to beige-brownish when denitrifying biofouling appeared on HDPE filter media. The color changed from yellow-white (sulfur-marble) to a little bit grayish-yellow when denitrifying biofouling appeared on a mixture of granular sulfur and marble chips.

The concentration of nitrates was measured by I-160 MI ionometer using an ELIS-121NO_3 ion-selective electrode. The range of measurements was $1\cdot10^{-1}...5\cdot10^{-5}$ M. The sensitivity was $5\cdot10^{-6}$ M. The concentration of dissolved oxygen in the nitrate-contaminated water was been measured by AZ 8402 oximeter. The value of pH was measured by I-160 MI ionometer with an ESK 10603 pH-sensitive electrode.

At mathematical processing and graphical display of the obtained results, the actual data of the measured values were calculated as the arithmetic average of three consecutive measurements. The correspondence between the model kinetic equations and the experimental data was checked by calculating the standard deviation between data arrays using Excel 2016 software.

Results and discussion

At the incubation, the appearance and growth of denitrifying biofouling inside HDPE and sulfur-marble filtration beds are accompanied by a decrease in the concentration of nitrate ions in the water (Fig. 1,A) and concurrent shift of pH (Fig. 1,B).

Denitrifying biofouling arisen inside of HDPE filter medium consumes nitrates much faster than they do it inside a mixture of sulfur and marble. This is because there are additives easily assimilated dissolved organic carbon (ethanol) for feeding heterotrophic bacteria in the water-filled HDPE, along with nitrates. Autotrophic denitrifying bacteria do not have so favorable conditions. The rate of their respiration and growth depends on the assimilation of the carbon from dissolved CO_2 or hydro-carbonates being in the water as the constituents of its mineral structure. Many genera of heterotrophic bacteria form powerful denitrifying biofoulings on different supports (surfaces) in the presence of an excess of nitrates and easily digestible organic substances [11]. Heterotrophic denitrification associated with the consumption of ethanol was described in work [2], where the following equations of bacterial respiration and constructive metabolism have been proposed:

$$12NO_3^- + 5C_2H_5OH \rightarrow 6N_2 + 10CO_2 + \\ + 9H_2O + 12OH^-; \quad (23)$$

$$97NO_3^- + 55C_2H_5OH + 15O_2 \rightarrow \\ \rightarrow 5C_2H_7O_2N + 85CO_2 + 99H_2O + \\ + 46N_2 + 97OH^-. \quad (24)$$

Taking the sum of (23) and (24), one gets:

$$109NO_3^- + 60C_2H_5OH + 15O_2 \rightarrow \\ \rightarrow 5C_2H_7O_2N + 95CO_2 + 108H_2O + \\ + 109OH^- + 52N_2 \quad (25)$$

or $$NO_3^- + 0.55C_2H_5OH + 0.137O_2 \rightarrow \\ \rightarrow 0.046C_5H_7O_2N + 0.87HCO_3^- + \\ + 0.99H_2O + 0.13OH^- + 0,477N_2. \quad (26)$$

Equation (26) depicts the «normalized» (recalculated with respect to one mole of NO_3^-)

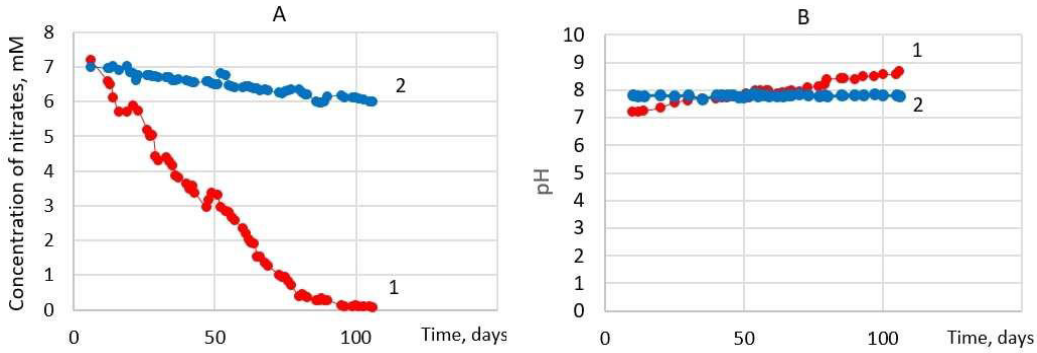

Fig. 1. A – Plot of the concentration of nitrate ions in the water vs. time at the incubation of denitrifying biofoulings on HDPE filter media (1) and the sulfur-marble mixture (2). B –Concurrent pH variation

heterotrophic denitrification with the absorption of ethanol. In this case, the stoichiometric $C/N-NO_3^-$ the ratio is 0.942. Denitrification leads to increment in biofuling growth ($C_5H_7O_2N$) of 0.046 M per 1 M of consumed NO_3^-. The reaction yields 0.87 M of HCO_3^-, 0.13 M of OH^- and 0.477 moles of nitrogen gas. Another equation of heterotrophic denitrification that describes the absorption of the about double quantity of ethanol per one mole of nitrate is as follows [5]:

$$NO_3^- + 0.943C_2H_5OH \rightarrow$$
$$\rightarrow 0.272C_5H_7O_2N + 0.511HCO_3^- +$$
$$+0.488OH^- + 1.372H_2O + 0.363N_2. \quad (27)$$

According to Eq. (27), biological denitrification leads to grow of biofouling which is equal to 0.046 M of $C_5H_7O_2N$ per 1 M of consumed NO_3^-. According to Eq. (27), the stoichiometric $C/N-NO_3^-$ ratio is 1.62. The process yields 0.511 M of HCO_3^-, 0.488 M of $OH^-$and 0.36 mole of nitrogen gas.

In the course of autotrophic denitrification, when sulfur is an electron donor and CO_2 is a source of assimilable carbon, Thiobacillus denitrificans [12] and Thiomicrospira denitrificans [13] dominate in biofouling. The reaction equations of autotrophic denitrification according to ref. [14] are as follows:

$$5S + 6NO_3^- + 2H_2O \rightarrow 3N_2 + 5SO_4^{-2} + 4H^+; \quad (28)$$

$$55S + 50NO_3^- + 38H_2O + 20CO_2 + 4NH_4^+ \rightarrow$$
$$\rightarrow 4C_5H_7O_2N + 25N_2 + 55SO_4^{-2} + 64H^+. \quad (29)$$

The sum of (28) and (29) is:

$$60S + 56NO_3^- + 40H_2O + 20CO_2 + 4NH_4^+ \rightarrow$$
$$\rightarrow 4C_5H_7O_2N + 28N_2 + 60SO_4^{-2} + 68H^+ \quad (30)$$

or $$NO_3^- + 1.071S + 0.714H_2O + 0.357CO_2 +$$
$$+0.071NH_4^+ \rightarrow 0.071C_5H_7O_2N +$$
$$+1.071SO_4^{-2} + 1.214H^+ + 0.5N_2. \quad (31)$$

According to Eq. (31), the autotrophic denitrification is accompanied by appearance of 0.071 M biomass and 0.5 moles of nitrogen gas per each mole of NO_3^- consumed. At the autotrophic denitrification, about 1.2 gram-equivalents of acid per one gram-equivalent of reduced nitrate is released. Limestone (marble), interacting with the released acid, ensures the stabilization of pH in water. The buffer capacity of denitrified water increases due to the formation of calcium bicarbonate:

$$2CaCO_3 + 2H^+ = Ca(HCO_3)_2 + Ca^{+2}. \quad (32)$$

The pH vs. time dependences for the incubation of denitrifying biofouling on the grains of the marble-sulfur mixture (Fig. 1,B, curve 2) confirm this conclusion.

The formation of denitrifying biofouling on HDPE filter media was considered as fully completed when the concentration of nitrate ions in the incubation water fell below the level of the sanitary and hygienic limit (<45 mg/L). This was reached by the end of the third month of the experiment. As for the concentration of nitrate ions in the water filling the bed of sulfur and marble mixture is concerned, it remained high (Fig. 1,A, curve 2). The incubation of colonies of denitrifying autotrophs continued for another three months.

The nitrate reduction by the incubated biofoulings was investigated on each carrier in U-shaped biofilters under two filtration modes: at a continuous flow in a closed-loop system and under the mode of displacement biofiltration (discrete pulses) in an open system. In the first case, the biofilters run on their water continuously pumped for treatment in a closed loop. In the second case, the portions of contaminated water were supplied into each biofilters periodically (every day in one gulp), and equal portions of the filtrate were got synchronously. At using displacement mode, the hydraulic retention time was set the same as at continuous flow mode.

Within the study of denitrification under continuous flow biofiltration mode in the closed-loop systems, the experimental details were as follows. The water with the initial nitrate concentration of 2.3 mM (195 mg L^{-1} $NaNO_3$+114 mg L^{-1} ethyl alcohol) was introduced into the device with an incubated HDPE filter medium. The water with the initial sodium nitrate concentration of 2.3 mM (195 mg L^{-1}, without alcohol) was introduced into the device with an incubated sulfur-marble filtration bed. This was done after thorough washing of filtration beds by the waters of the said composition. Then, the concentration of nitrates was measured daily at the exit of biofilters in a long-continued

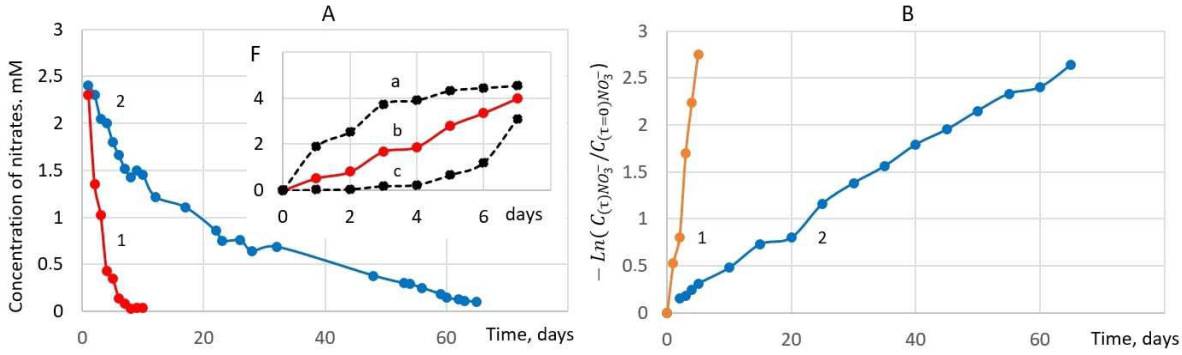

Fig. 2. A – Kinetic curves of the heterotrophic (1) and autotrophic (2) denitrification at the continuous flow of nitrate-contaminated water in a closed-loop of U-shaped bio-filters. The inset in Fig. 2,A displays curve 1 replotted in coordinates $F=2(C_0-C_t)$ vs. τ, $F=-\ln(C_t/C_0)$ vs. τ, and $F=0.1(1/C_t-1/C_0)$ vs. τ. B – Transform of the experimental data presented in Fig. 1,A by using semi-logarithmic coordinates

experiment with the rates of water pumping of 0.029 mL s^{-1} (2.5 liters per day) through HDPE filter media and 0.02 mL s^{-1} (1.7 liters per day) through the sulfur-marble filtration bed. The kinetics of heterotrophic and autotrophic denitrification at the continuous-flow biofiltration in the closed-loop of U-shaped biofilters is shown in Fig. 2,A (curves 1 and 2). The treatment of these experimental data by means of Eqs. (14)–(16) allows evaluating the order of reactions of nitrates ions reduction producing gaseous nitrogen. The results are shown in the inset in Fig. 2,A.

Curve 1 in Fig. 2,A was replotted in coordinates $F=2(C_0-C_t)$ vs. τ, $F=-\ln(C_t/C_0)$ vs. τ and $F=0.1(1/C_t-1/C_0)$ vs. τ. In those coordinates, the experimental kinetic curves should transform into straight lines indicating zero, first, or second-order reactions, respectively. As can be seen, only the plot $F=-\ln(C_t/C_0)$ vs. τ fits evaluation criteria; thus, the process obeys the kinetics of a first-order reaction. The result allows concluding a uniform distribution of denitrifying biofilms upon surfaces of porous space when biofilters start to run. Figure 2,B reflects the logarithms of ratios of current concentrations of nitrates to their initial concentration vs. time for extended biofiltration duration. These data confirm the first order of reactions nitrates reduction in the performed experiments.

Reaction rate constants calculated from the slopes of the graphs in Fig. 2,B are equal to 0.56 day^{-1} ($6.48\cdot10^{-6}$ s^{-1}) and 0.046 day^{-1} ($5.32\cdot10^{-7}$ s^{-1}) for heterotrophic and autotrophic denitrification, respectively. The rate of heterotrophic denitrification is approximately 12 times higher than the rate of autotrophic denitrification. When the initial concentration of nitrate ions in the inlet water is 2.3 mM, the retention time of NO_3^- inside of each examined biofiltration beds should be about 5 and 50 days, respectively, to achieve physiologically safe concentrations of nitrate ions at the exit of biofilters (45 mg L^{-1}).

A feature that makes difficult the use of continuous-flow biofiltration in the home-use devices is the clogging of the biofiltration bed.

The problem may be overcome, if the periodical displacement mode is used instead of continuous flow biofiltration. In our study, 2.5 liters of water with a chosen nitrates concentration and required additive of ethyl alcohol were fed to the apparatus with HDPE filter media each day in one gulp; and 1.7 liters of water with the same nitrates concentration were added to the apparatus with the mixture of sulfur and marble. This is because the volume ratio of pore spaces in used filtration downloads is equal to one and a half to one. With the supplying by designated portions of nitrates-contaminated water to the processing, equal portions of the water with a lower concentration of nitrates were synchronously released in one gulp at the exit of biofilters. The results obtained under displacement biofiltration mode with using of HDPE filter media (heterotrophic denitrification) are shown in Fig. 3. In this experiment, the preconditions of biofiltration were as follows. Initially, the biofiltration bed was washed with nitrate-contaminated water (the concentration of $NaNO_3$=280 mg/L together with the required amount of ethanol) so that the concentration of NO_3^- ions at its input and output has become the same. Then, two and a half liters of water (with the concentration of $NaNO_3$=280–300 mg/L together with the required amount of ethanol) were poured into the biofilter in one gulp every day, and the concentration of nitrate ions was measured in the synchronously released filtrate. Solid line segments

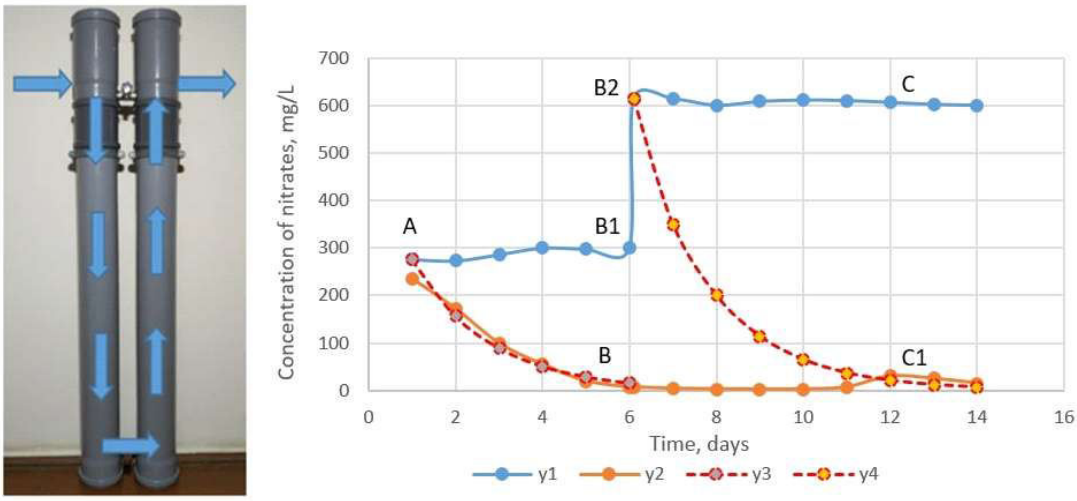

Fig. 3. Photo of U-shaped biofilter and kinetics of water denitrification in it at displacement biofiltration. Water was supplied daily by portions of 2.5 liters; y1 is the concentration of nitrate ions in the supplied portions of water; y2 is the concentration of nitrate ions in the portions of the filtrate; y3 and y4 show the results of calculations according to Eq. (21)

AB1 (concentration of nitrates in the entering water) and AB (concentration of nitrates in the received filtrate) in the graphs of Fig. 3 correspond to this part of the study.

Processing of the experimental data from the segment AB (Fig. 3) according to Eq. (21) gave the value K=0.56 day^{-1}, which confirms that the changes in concentration of nitrate ions measured at the exit of the biofilter obey the first-order reaction kinetics of biological denitrification.

After the concentration of nitrate ions in the portions of denitrified water has come close to zero (as depicted by the point B in Fig. 3), the concentration of sodium nitrate in subsequent portions of water supplied to the displacement biofiltration was increased to 600 mg L^{-1}. This is shown by the vertical line segment B1−B2. After six days of the ongoing experiment, the transition to new conditions of biofiltration led to a small increase in the concentration of nitrate ions in the filtrate. This reflects the point C1 at the end of the line segment BC1. The result is consistent with the calculated decrease in the concentration of nitrate ions in the filtrate (dashed curve B2−C1) according to Eq. (21) if k=0.56 day^{-1}.

Conclusions

The biofiltration in the displacement mode is an alternative to the direct flow filtration. At using the displacement mode, nitrate-contaminated water is fed by separate portions (in one gulp) to the inlet of the bio-filter. At the same time, an equal quantity of denitrified water is released from the biofilters exit. The portions are selected so that their hydraulic retention time inside the filter body provides the desired concentration of nitrate ions at the filter's outlet.

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ДЕНІТРИФІКАЦІЯ ВОДИ МЕТОДОМ ВИТИСНЮВАЛЬНОЇ БІОФІЛЬТРАЦІЇ

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Мета роботи – створити простий і надійний біофільтр для децентралізованого очищення води, що забруднена нітратами. Денітрифікація питної води вивчалася методом витиснювальної (поршневої) біофільтрації в спеціально розроблених пристроях, призначених для індивідуального використання. При певних розмірах зерен біофільтраційного шару і напрямків потоків фільтрації зміна режиму роботи денітрифікаційного біофільтра з прямоточного на витиснювальний дає суттєві переваги. Непотрібно підтримувати безперервний, повільний потік води крізь біофільтр. Споживач одержує можливість подавати великі порції води в біофільтр залпом (імпульсом) і одночасно отримувати таку ж кількість денітрифікованої води. Конструкція створених біофільтрів проста. При виготовленні цих біофільтрів можна використовувати матеріали з мінімальним «вуглецевим відбитком».

Ключові слова: біофільтрація, режим витіснення, питна вода, видалення нітратів, децентралізоване водопостачання, очищення води.

WATER DENITRIFICATION BY DISPLACEMENT BIOFILTRATION

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This work was aimed creating a simple and reliable submersed biofilter for the decentralized treatment of nitrate-contaminated water. Denitrification of water was studied by the method of displacement (piston) bio-filtration in specially designed devices intended for home application. At certain sizes of grains of bio-filtration bed and filtration flow directions in it, the change in operating mode of denitrifying biofilter from direct flow to displacement mode offers the following advantages. There is no need to maintain a continuous and slow flow of water through the biofilter. The consumers have the opportunity to feed big portions of water into the bio-filter in one gulp (pulse) and nevertheless get the same quantity of denitrified water. The design of created biofilters is simple. Assembling these bio-filters implies the use of materials with a minimum carbon footprint.

Keywords: biofiltration; displacement mode; drinking water; removal of nitrates; water purification.

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