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Buffer Effects in Submersed Denitrifying Biofilter

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ABSTRACT

The high content of nitrates in drinking water leads to serious diseases. The creation of biofiltering devices with the longest time of their operation between preventive flushes is extremely important. The purpose of this study was to investigate the features of the functioning of the developed U-shaped submersible denitrifying biofilter during its long-term operation in the piston filtration mode. The denitrification of water by using the method of displacement (piston) biofiltration in a submersible small U-shaped biofilter with immovable carriers of attached microflora in its filter load was studied. As a result, clogging of the pore space of the biofilter in the zone of excess bacterial nutrition is prevented and the vital activity of bacteria is maintained in places where there is no nutrient substrate. It has been shown that, due to adaptive mechanisms, denitrifying bacteria convert nitrate ions into gaseous nitrogen, consuming extracellular polymeric substances. The rate constants of the reaction of reduction of nitrates to molecular nitrogen in different zones of the biofilter under different filtration modes were determined. The activity of the microflora in-side the biofilter quickly returns to its original level when a full-fledged external nutrition is resumed. The efficiency of nitrate to nitrogen conversion in the studied biofilter is $94.2\pm 8.9\%$.

Keywords: biofiltration, denitrification, microflora activity, self-regulation, systemstability.

INTRODUCTION

Pollution of drinking water sources with nitrates has become a planetary problem. It is becoming rampant in many countries [Abascal et al., 2022]. Elevated concentrations of nitrates in drinking water cause serious diseases [Ward et al. 2018]. Due to violations of nitrogen metabolism in recipients, the reproductive function worsens and the incidence of congenital pathologies in newborns increases [Brender et al. 2016; Sherris et al. 2021]. Infants develop methemoglobinemia [Martínez de Zabarte Fernández et al. 2018]. Long-term intake of nitrates in the human body in excess doses reduces its resistance to the effects of blastomogenic and mutagenic factors [Taneja et al., 2017; Richards et al., 2022].

Nitrates are characterized by their high solubility and weak adsorption by water-bearing rocks. This contributes to the migration of nitrates over long distances with water flows and their accumulation in aquifers [Bastania et al., 2019]. Nitrates enter surface and groundwater from sources of natural and anthropogenic origin. Studies have shown that nitrate pollution of surface and groundwater can occur simultaneously from various sources [Abascal et al., 2022]. This process is multifactorial, difficult to monitor, characterized by prolonged consequences and involves the development of measures as well as decision-making tools to manage water pollution [Jia Xin et al. 2021]. Currently, dangerous concentrations of nitrates in water sources are observed in various countries [Shrestha et al., 2016; Adimalla et al., 2019; Roshanravan et al. 2021].

Removal of nitrates from drinking water is carried out centrally, locally or individually. The work [Jensen et al., 2014] provides an overview of the methods and technologies for removing nitrates. In Pirsaheb et al. [2016], Sharma et al. [2017], Matei et al. [2021] the advantages and disadvantages of different methods were discussed.

With centralized water purification from nitrates, physical and chemical processes are used, such as ion exchange, reverse osmosis, electrodialysis, catalysis [Jensen et al., 2014; Ruiz-Beviá F., et al, 2019]. Drinking water treatment plants often use combined technologies, for example, the integration of electrodialysis with biological denitrification allows the purification and disposal of brines [Cheikh et al., 2013]. Hybridization of catalysis and ion exchange helps to reduce the cost of regenerating solutions for ion exchange resins [Kim et al., 2016; Bergquist Allison et al., 2016], technologies for nitrate hydrogenation in the presence of mono- and bimetallic catalysts are being developed, evaluated by [Marchesini et al., 2019; Tokazhanov et al., 2020] their reactivity, N2 selectivity, and durability.

Biological denitrification methods are considered promising [Khera et al., 2021]. Biological denitrification results in minimal carbon emissions into the biosphere [Blackburn et al., 2021]. A number of studies describe the use of microbiological cleaning [Issayeva et al., 2022], incl. denitrification for treatment of centralized wastewater [Mohseni-Bandpi et al., 2013], but so far this method has not been widely used for decentralized water treatment [Brown et al., 2015; Kirisits et al., 2019; Khera et al., 2020]. The results of studies on autonomous denitrifying devices with movable and movable carriers of attached microflora, which operate both in continuous and periodic modes, were described [Alyamani et al., 2020; Lin et al., 2020].

Biological membrane filters [Simonič et al., 2017], where denitrification occurs under anoxic and anaerobic conditions, are also being developed. They exploit the denitrifying abilities of autochthonous microorganisms, which split off oxygen from nitrate ions and use it for their respiration. At the same time, bacteria receive energy from nutrient substrates – sources of assimilated carbon and electron donors, the best of which is ethanol. In attached growth systems, colonies of denitrifying bacteria function on inert carriers (slag, sand, gravel, expanded clay, plastic, synthetic fabrics, etc.), with the formation of biofilms, which further grow into powerful conglomerates. Conglomerates represent accumulations of bacteria in the matrix of hydrated extracellular polymeric substances (EPS) created by them, which consists of polysaccharides, proteins, lipids, etc. and ensures their adhesion to surfaces [Flemming et al., 2010].

The disadvantage of biological filtration in submersible biofilters with attached microflora on immovable carriers is the clogging (clotting) of the filter with growing biomass. Such biofouling reduces the efficiency of biofiltration, increases the likelihood of channel formation and the ingress of biomass fragments (flocculi, plankton particles) into the treated water (leachate). To remove excess biomass, it is necessary to regularly flush the biofilter, which is considered a critical factor. In this regard, an urgent task is to create the biofilter devices with the longest possible time of their operation between preventive flushes [Rocher et al., 2019]. In addition, the use of submersible denitrifying biofilters with water purification in the displacement (piston) biofiltration mode seems promising. In this mode, a biofilter with a filtering load of a certain configuration is fed in one gulp of a portion of water for biofiltration and synchronously receives denitrified water, according to a given algorithm. A submersible biofilter with attached biomass has been developed, operated in a piston mode for supplying water to biofiltration, which can be operated without preventive washing for a year or more [Gevod et al., 2021]. Despite the successful operation, a number of issues have arisen that require more detailed study:

- assessment of the biofilter for sustainable provision of a given degree of nitrate removal from treated water in the event of a temporary interruption of the nutrient substrate supply or suspension of biofiltration;
- study of changes in the rates of conversion of nitrate ions into nitrogen in the body of the bio-filter, depending on the conditions of feeding its denitrifying microflora with ethanol and the regime of water supply for biofiltration.
- use of equations of formal kinetics to determine the influence of biofiltration conditions on the redistribution of zones of bacterial activity inside the biofilter.

On the basis of these issues, the purpose of this study was to investigate the features of the

functioning of the created U-shaped submersible denitrifying biofilter during its long-term operation in the piston filtration mode.

MATERIALS AND METHODS

Small submersible biofilter

The object of the study was a small submersible U-shaped biofilter. Its body (Fig. 1) was made of standard PVC pipes with a height of 1500 mm and an internal diameter of 100 mm. The bottoms of the knees are muffled. Between the knees, at a distance of 50 mm from the bottoms, a hydraulic jumper with an exhaust valve is mounted. In the upper parts of the elbows, at a distance of 200 mm from the ends, branch pipes are installed for



Figure 1. General view of the biofilter and the direction of movement of the filtered water in it; 1 -water supply for filtration; 2 -point of water sampling after 24 hours of filtration; 3 -water sampling point after filtration; 4 -filtered water outlet

supplying water for filtration and for collecting filtered water.

The water sent for biofiltration was a model solution prepared with tap water. Solution composition: 185 ± 5 mg of sodium nitrate per 1 dm³ of tap water. The filter bed consisted of 16x12 mm HDPE filter media webbed polymer rollers with denitrifying bacteria grown on their surface. Water sampling for analysis was carried out from three points (points 2, 3, 4). In portions of water supplied to the biofilter, the ratio (N/C) corresponded to the stoichiometric equation of denitrification and was 1/1.5. The direction of movement of portions of denitrified water in the biofilter is shown by arrows in Figure 1.

Methodology

The biofilter was inoculated with sapropel r. Dnieper for the effective use of autochthonous microflora [Khera et al., 2021]. Incubation of biofouling on the elements of the filter media was carried out for 180 days at a temperature of $21\pm2^{\circ}$ C, pH varied from 7.8 to 8.6 [Gevod et al., 2021]. In the biofilter, the conditions were created for the process of anoxic, anaerobic biofiltration [Rodríguez-Escales, 2016].

Ethanol was used as electron donors (DSTU 4221:2003). Its choice was due to its availability, low toxicity (there are no restrictions on the content of ethanol in drinking water), good knowledge, and complete conversion of nitrate ions into molecular nitrogen.

The experimental procedure included the study of the denitrification process under the conditions of regular (daily), irregular (with a break for several days) and reverse supply of treated water (model solution) to the biofilter.

The supply of purified water to the inlet of the biofilter (position 1) was carried out in portions of a "volley" of 5 liters, each with synchronous production of the same amount of denitrified water at the outlet from position 4.

The activity of the denitrifying microflora in the biofilter was assessed depending on the concentration of the nutrient substrate (ethanol) and monitored by the dynamics of changes in the concentration of nitrate ions in the water spaces of the inlet (point 2) and outlet (point 3) compartments of the knees of the biofilter (Figure 1).

The concentration of nitrate ions in the source water (pos.1) asked a constant. Nitrate concentrations were measured continuously (the study of formal kinetics in a given place for a given period of time) and daily at a given time when performing a chronic study.

The content of nitrate ions was measured with an I-160MI ion meter with an ELIS-121 NO3⁻ membrane nitrate-selective electrode and an EV-L1MZ.1 silver chloride reference electrode. In the experiments with duration of up to 10 days, the measurement of the concentration of nitrate ions in the aquatic environment of the inlet and outlet sections of the biofilter and the accumulation of the information obtained were carried out automatically, according to the specified algorithm of the Analytics program.

Processing of experimental data. The method was chosen based on the fact that the kinetics of microbiological processes in a formalized form adequately describes the Monod model by a system of partial differential equations, as presented below [Lee et al., 2006; Calderer et al., 2010]:

$$\frac{\partial [ED]}{\partial \tau} = -k_{max} \left\{ \frac{[ED]}{[ED] + K_{SED}} \right\} \left\{ \frac{[EA]}{[EA] + K_{SEA}} \right\} [X] (1)$$

$$\frac{\partial[EA]}{\partial\tau} = Q \frac{\partial[ED]}{\partial\tau}$$
(2)

$$\frac{\partial[X]}{\partial\tau} = -Y_h \frac{\partial[ED]}{\partial\tau} - b[X] \tag{3}$$

where: $\partial [ED]/\partial \tau$ – the rate of the process (mol/ dm³.sec) in relation to the concentration of the substance, which is an electron donor and a source of digestible carbon; [ED] – the concentration of the elecdonor substance tron $(mol/dm^3);$ $\partial [EA]/\partial \tau$ -the rate of the process (mol/dm³. sec) in relation to the concentration of the substance, which is an electron acceptor; [EA] – the concentration of the electron acceptor substance (mol/dm³); [X] – the concentration of active bacterial cells (mol/dm³); Y_h – microbial growth; Q – the stoichiometric coefficient; k_{max} – the maximum (limiting) rate (sec⁻ ¹) of the absorption of a substance - an electron donor; b is the kinetic coefficient of biomass concentration decrease due to its endogenous destruction; $K_{\rm SED}$ and $K_{\rm SEA}$ – the concentrations of substances - donors and acceptors of electrons at which the rates of processes are half of their maximum possible value.

Equations (1)–(3) reveal the dynamics of the interaction of substances in a microbiological system. To obtain reliable information, it is required to have the numerical values of all coefficients and concentrations included in (1)–(3). The task is simplified, if the influence of the main factors is considered separately. In particular, studying the denitrification of water in the mode of displacement (piston) biofiltration, [Gevod V.S., et al., 2021] it is possible to follow the dynamics of changes in the concentration of nitrate ions in the biofiltrate under certain conditions. For example, depending on the hydraulic residence time of portions of denitrified water inside the biofilter at such concentrations of electron donor substances and active biomass, which in the Monod system of equations give a correction to the value of k_{max} as constant factors, then the partial differential equations of the Monod model are reduced to a simple form of the Michaelis-Menten differential equation, that is:

$$\frac{\partial [EA]}{\partial \tau} = -k_{max} \frac{[EA]}{[EA] + K_{SEA}} \tag{4}$$

Here [EA] is the current concentration of nitrate ions in the aquatic environment of the biofilter, k_{max} is the limiting speed of the process according to the Michaelis-Menten model, K_{SEA} is the concentration of the substance – electron acceptor (nitrate ions), at which the process speed is half of its maximum possible value.

Within the framework of (4), it is advisable to process the results of experiments using the integral form of the Michaelis-Menten equation. This eliminates the need to differentiate the initial experimental dependences "concentration – time" to obtain the dependences "velocity – time" with their subsequent processing as indicated above. Integrating equation (4) over $[EA_0]$ to [EA] and from 0 to τ gives:

$$-\int_{0}^{\tau} d\tau = \int_{[EA_{0}]}^{[EA]} \frac{K_{SEA}}{k_{max}} \frac{d[EA]}{[EA]} + \int_{[EA_{0}]}^{[EA]} \frac{1}{k_{max}} d[EA]$$
(5)

and:

$$-\tau = \frac{K_{SEA}}{k_{max}} \ln \frac{[EA]}{[EA_0]} + \frac{1}{k_{max}} \left(\left[[EA] - [EA_0] \right] \right)$$
(6)

or:

$$\frac{[EA] - [EA_0]}{\tau} = k_{max} - \frac{K_{SEA}}{\tau} \ln \frac{[EA_0]}{[EA]} \quad (7)$$

On the basis of (7), plotting in coordinates $([EA_0]-[EA])/\tau$ (ordinate) and $1/\tau^*\ln([EA_0]/[EA])$ (abscissa) allows find the values of k_{max} and K_{SEA} by the slope of the resulting straight line relative to the abscissa axis and by its intersection with the ordinate axis.

In accordance with (4), there may be such conditions that $K_{SEA} \gg [EA]$. Then, the result of processing the experimental data in the form of a function $\ln([EA_0]/[EA])$ of τ also gives a straight line. Linearization indicates the kinetics of the reaction of the first order relative to [EA], where the value of the reaction rate constant (*K*), determined by the slope of the obtained straight line relative to the abscissa, is equal to the ratio k_{max} / K_{SEA} . Using the integral form of equation (4), it is possible to process experimental data in the coordinates $\ln\{([EA_0]-[EA])/[EA_0])\}$ of τ , which reflects the degree of conversion of the initial substance into the reaction product.

RESULTS AND DISCUSSION

In the created biofilter, the denitrifying microflora reacts to changing conditions of its existence. An interruption in the supply of water for biofiltration for a long time, or intensive washing of the biofilter load, creates such a "stress" effect on the colonies of denitrifying bacteria in the body of the biofilter that in the initial period of its subsequent operation, the kinetics of the process corresponds to a first-order reaction with a rate constant of approximately 0, 56 days⁻¹ [Gevod V.S., et al., 2021]. Then, the denitrification rate increases in the upper part of the biofilter inlet leg, and the rate constant for the conversion of nitrate ions to nitrogen there reaches 1.4 day⁻¹.

The U-shaped biofilter is a symmetrical design. Therefore, it was important to trace how the reverse supply of portions of water to this device affects the activity of the denitrifying microflora in its inlet (Fig. 1, point 1) and outlet (point 4) knees changing places. Figure 2 presents the results of the change (reverse) of the supply of water portions to the biofilter on the activity (performance) of the denitrifying microflora in its input and output turn.

The lines of the graphs show that displacement biofiltration, when carried out in the "forward" direction, is characterized under stationary conditions by a rapid decrease in the concentration of nitrate ions in the water of the receiving compartment of the biofilter inlet elbow (curve 2, Fig. 2a). Instrumental measurements for constructing this curve were conducted automatically every 10 minutes according to the signals of the Analytics algorithm throughout the day, from the moment the next portion of water was supplied to the biofilter for processing. At the same time, the concentration of nitrate ions, which was measured daily at the biofilter outlet, was as shown (line 3, Fig. 2a). The concentration of nitrate ions in the water supplied to the biofiltration, remained



Figure 2. The effect of changing (reversing) the supply of water portions to the biofilter on the activity (performance) of the denitrifying microflora in its input and output knees; where: $1 - \text{concentration of nitrate ions in the water supplied for filtration; } 2 - \text{concentration of nitrate ions in the inlet knee of the biofilter in stationary mode; } 3 - \text{concentration of nitrate ions in filtered water; } 4 - \text{concentration of nitrate ions in the outlet turn after changing the direction (reverse) of water supply for biofiltration; 5 - concentration of nitrate ions in the outlet leg in stationary mode)$

constant (line 1, Fig. 2a). When reversing in the direction of biofiltration with daily supply of portions of water to the outlet compartment of the biofilter and continuous automatic monitoring of the dynamics of the decrease in the concentration of nitrate ions in this compartment, the picture changes. First, the results are shown in Fig. 2b by line 4. However, over time, the course of the curve becomes more and more steep. Upon reaching the stationary state, the result becomes as shown in Fig. 2b by line 5. Its course repeats the course of line 2 in Fig. 2a. It follows that denitrifying heterotrophs concentrate and manifest themselves in an equivalent way in those zones of the biofilter where environmental conditions are equally favorable for them. When the direction of displacement biofiltration is reversed, the zone of best conditions for nutrition and respiration is moved from the inlet leg of the biofilter to its outlet leg. Bacteria quickly react to this, and the rate of denitrification there increases dramatically. The denitrification rate constant in the upper part of the knee, which became the entrance to the biofilter, reaches a value of 1.4 day⁻¹, and in the upper part of the opposite knee (i.e. the knee from which the biofiltrate flows), it decreases to a value of 0.56 day⁻¹.

The reaction of the denitrifying microflora in the biofilter to the conditions of its nutrition (removal of the ethanol additive from the water supplied to the biofiltration) also deserves attention. Figure 3 shows the dynamics of the reaction of the denitrifying microflora in the biofilter to the changes in the conditions of its nutrition. Sector "0–A" presents the time dependences of the changes in the concentration of nitrate ions in the treated water of the input "2" and output "3" compartments of the biofilter in response to the daily supply of portions of water to the biofilter with the addition of the optimal amount of ethanol to it. As noted above, it was a 1.5 times excess compared to the stoichiometrically necessary for the conversion of nitrate nitrogen into molecular nitrogen [Mohseni-Bandpi et al., 2013; Rodriguez-Escales et al., 2016].

Dashed arrows show that the concentration of nitrate ions was measured daily before the next new portion of water was fed to biofiltration. It can be seen that under such conditions of bacterial nutrition, the biofilter provides a decrease in the concentration of nitrate ions in denitrified water from the initial $185.0 \pm 15.1 \text{ mg/dm}^3$ at its inlet to the final values of no more than $10.0 \pm 1.0 \text{ mg/}$ dm³ (94.2 ±8.9%) at output.

Sector "A–B" shows the same dependences, but obtained in response to the daily supply of portions of water containing nitrate without the addition of ethanol to the biofilter. The transition to such a biofiltration mode is indicated by a vertical arrow with the index "A". Already a day after the cessation of the supply of ethanol to the denitrified water, the concentration of nitrate ions begins to increase in the inlet section of the inlet knee of the biofilter, which is tracked in the



Figure 3. Dynamics of the response of denitrifying microflora in a biofilter to changes in its nutritional conditions; where: 1 - concentration of nitrate ions in water supplied to biofiltration; 2 - concentration of nitrate ions in the inlet section of leg "2"; 3 - concentration of nitrate ions in the outlet section of leg "3". Concentrations 2 and 3 were measured daily before the next portion of water was supplied for biofiltration treatment

chronology of the supply of successive portions of water for denitrification. The process develops as curve 2 in the selected fragment demonstrates. By the 25th day of continued operation of the biofilter with regular supply of portions of water to it without the addition of ethanol, the concentration of nitrate ions in the inlet compartment of the inlet knee of the biofilter ceases to differ from the concentration of nitrate ions in the water supplied to the biofiltration (line 2 comes close to line 1). At the same time, at the outlet of the biofilter, the concentration of nitrate ions changes as shown by line 3. Denitrification along the biofiltration trajectory continues due to the use of exopolysaccharides by bacterial cells from their own mucous secretions. This is indicated by the course of the kinetic curve 3 within the time interval of 24–34 days. It is similar to the course of the kinetic curve 2 within the time interval of 10–25 days.

The result of processing the kinetic dependences of the reaction of the denitrifying microflora in the biofilter to a change under the conditions of its nutrition is shown in Figure 4.

Processing of the experimental data presented in Figure 3 in semi-logarithmic coordinates, reveals in the sector "A–B" two straight segments with the same slopes, relative to the abscissa axis. This indicates the first order of the reaction of inhibition of water denitrification by heterotrophic microflora in response to the cessation of the supply of an easily digestible nutrient substrate, ethanol, to the purified water. Under such conditions, denitrification continues only due to the use of an internal energy resource by bacteria - extracellular polymeric substances from their own mucous secretions. Bacterial cells intensively produce mucous secretions around themselves when nutrient substrates in the aquatic environment are in excess, as described in [Flemming et al., 2010]. The rate constant of the process of "braking" the conversion of nitrate ions into molecular nitrogen is 0.15 day⁻¹.

Restoration of the initial conditions of nutrition of heterotrophic microflora in the inlet knee of the biofilter returns the activity of denitrifying heterotrophs to the level that preceded the cessation of nutrition. This is demonstrated by the dynamics of the decrease in the concentration of nitrate ions in the "B–C" section. The vertical arrow with index B is the moment of return to full nutrition of the denitrifying microflora in the biofilter with the addition of ethanol to the supplied water.

Denitrifying bacteria also react to the changes in the biofiltration mode, when, after a long period of operation of this device with regular supply of portions of water to its inlet and with an optimal ethanol content in it, a stage begins with interruptions in the supply of water for biofiltration and the cessation of adding ethanol. The reaction of denitrifying microflora to a change in the biofiltration regime is shown in Figure 5.

Here, line 1 displays the mode of supplying portions of water to displacement biofiltration. The concentration of nitrate ions in the supplied portions was $(185 \pm 5 \text{ mg/dm}^3)$, the volume was 5.0 dm³. Ethanol was not supplied to these portions as an external power source. The highlighted



Figure 4. The result of processing the kinetic dependences of the reaction of the denitrifying microflora in the biofilter to a change in the conditions of its nutrition



Figure 5. The reaction of denitrifying microflora to a change in the biofiltration regime, where: 1 - concentration of nitrate ions in water periodically supplied to biofiltration; 2 - increase and decrease in the concentration of nitrate ions in the inlet compartment of the inlet knee of the biofilter with periodic water supply; 3 - concentration of nitrate ions in the outlet section of the inlet leg

areas with indices "0" in the figure field indicate periods of interruption of the supply of water portions for displacement biofiltration. The points on the lines of the graph (Fig. 5a) correspond to the days when the concentration of nitrate ions was measured in the water supplied to the biofiltration (1), as well as in the water of the inlet compartment in the inlet bend of the biofilter (line 2) and in the water of the outlet compartment in the outlet bend biofilter (line 3). The concentration of nitrate ions in the resulting biofiltrate, which is identical to the concentration in the outlet compartment (3) of the outlet knee of the biofilter, did not exceed 10 mg/dm³ and was provided by the presence of its own extracellular polysaccharides as a source of nutrition, approximately 94%.

From the obtained results it follows that in the absence of external power supply the suspension of the supply of portions of water to the displacement biofiltration does not lead to the termination of the process of biological denitrification of the water remaining in the biofilter. At the same time, the functioning of the denitrifying microflora in the filter media continues. However, curve 2 of the increase in the concentration of nitrates after the resumption of the supply of portions of water for purification indicates a gradual exhaustion of the "internal" food resource.

The shape of the descending branches on curve 2 in the selected zones with indices "0" indicates an inversely exponential dependence of the decrease in the concentration of nitrate ions on time in the still water of the inlet compartment in the inlet knee of the biofilter. Graphs of the logarithm of the concentration of nitrate ions plotted against time for the selected intervals are shown in Figure 5b. Their approximately linear course gives the reason to believe that denitrification using the "internal" resource of nutrition – its own extracellular polysaccharides – occurs in accordance with the concept of a first-order reaction. The value of the process rate constant, calculated from the slope of the trend line of these graphs, is 0.55 day⁻¹.

CONCLUSIONS

Filter bed clogging management is one of the key challenges in the biological denitrification process. It is especially difficult to implement in decentralized treatment of nitrate-containing drinking water in POUs operating in direct flow mode. The process of displacement (piston) biofiltration in the proposed filter U-shaped design may be an alternative. A distinctive feature of the functioning of the biofilter is that the denitrifying microflora tends to adapt to the changes in the biofiltration regimes, especially to the regularity of the supply of treated water and organic carbon to the biofilter, as an element of external nutrition. The studies of the conversion of nitrates to nitrogen in the filter media of the biofilter showed that the microbial community manifests itself as a self-regulating system, and its activity is supported by the presence of an internal source of nutrition by extracellular polymeric substances. Piston water supply for filtration, accompanied

by hydraulic vibrations and the use of biofouling, increase both the resistance of the filter load to clogging (colmatation) and the stability of the biofilter itself. At the same time, the efficiency of the denitrification process is $94.2 \pm 8.9\%$. In addition, the proposed biofilter does not have the operation of pumping the purified water, which reduces the operating costs when using it. It was shown that the occurrence of "buffer" zones in the biofilter array provides an increase in the stability of the biofilter. This is expressed in obtaining a biofiltrate with the desired quality indicators, regardless of emergency situations, such as a temporary cessation of ethanol dosages or water supply for biofiltration. The experimental approach used in this study can be applied to scale up a fixed biofilm biofilter in removing nitrate from drinking water.

REFERENCES

- Abascal E., Gómez-Coma L., Ortiz I., Ortiz A., 2022. Global diagnosis of nitrate pollution in groundwater and review of removal technologies. Science of The Total Environment, 810, 152233. https://doi. org/10.1016/j.scitotenv.2021.152233
- Adimalla N., Qian H. 2019. Groundwater quality evaluation using water quality index (WQI) for drinking purposes and human health risk (HHR) assessment in an agricultural region of Nanganur, south India. Ecotoxicology and environmental safety, 176, 153–161. https://doi.org/10.1016/j. ecoenv.2019.03.066
- Alyamani E.J., Booq R.Y., Bahkali A.H., Alharbi S.A. 2020. Biological Removal of Nitrates from Groundwater Resources in Saudi Arabia. J Pure Appl Microbiol, 14(3), 2203–2213. https://doi. org/10.22207/JPAM.14.3.61
- Bastani M., Harter T. 2019. Source area management practices as remediation tool to address groundwater nitrate pollution in drinking supply wells. Journal of Contaminant Hydrology, 226, 103521. https://doi. org/10.1016/j.jconhyd.2019.103521
- Bergquist A.M., Choe Jong K., Strathmann T.J., Werth C.J. 2016. Evaluation of a hybrid ion exchange-catalyst treatment technology for nitrate removal from drinking water. WaterResearch, 96, 177– 187. https://doi.org/10.1016/j.watres.2016.03.054
- Blackburn E.A.J., Emelko M.B., Dickson-Anderson S., Stone M. 2021. Advancing on the promises of techno-ecological nature-based solutions: A framework for green technology in water supply and treatment. Blue-Green Systems, 3(1), 81–94. https://doi. org/10.2166/bgs.2021.008

- Brender J.D., Weyer P.J. 2016. Agricultural Compounds in Water and Birth Defects. Curr Environ Health Rep., 3(2), 144–152. https://doi.org/10.1007/ s40572-016-0085-0
- Brown J., Summers R.S., Le Chevallier M., Collins H., Roberson J.A., Hubbs S., Dickenson E. 2015. Biological Drinking Water Treatment? Naturally. Journal American Water Works Association, 12(107), 20–30. https://doi.org/10.5942/ jawwa.2015.107.0183
- Calderer M., Jubany I., Pérez R., Martí V., de Pablo J. 2010. Modelling enhanced groundwater denitrification in batch micrococosm tests. Chem. Eng. J., 165(1), 2–9. https://doi.org/10.1016/j. cej.2010.08.042
- Cheikh A., Grib H., Drouiche N., Abdi N., Lounici H., Mameri N. 2013. Water denitrification by a hybrid process combining a new bioreactor and convention a lelectro dialysis, Chemical Engineeringand Processing: Process Intensification, 63, 1–6. https://doi.org/10.1016/j.cep.2012.11.004
- Flemming H.C., Wingender J. 2010. The biofilm matrix. Nature reviews. Microbiology, 8(9), 623– 633. https://doi.org/10.1038/nrmicro2415
- 12. Gevod V.S., A.S. Chernova A.S. 2021. Water denitrification by displacement biofiltration: transition of designed biofilter to the stationary mode. Voprosykhimiiikhimicheskoitekhnologii, 4, 21–26. https:// doi.org/10.32434/0321-4095-2021-137-4-21-26
- Jensen V.B., Darby J.L., Seidel C., Gorman C. 2014. Nitrate in Potable Water Supplies: Alternative Management Strategies, Critical Reviews in Environmental Science and Technology, 44(20), 2203–2286. https://doi.org/10.1080/10643389.2 013.828272
- Xin J., Wang Y., Shen Z., Liu Y., Wang H., Zheng X. 2021. Critical review of measures and decision support tools for groundwater nitrate management: A surface-to-groundwater profile perspective. Journal of Hydrology, 598, 126386. https://doi. org/10.1016/j.jhydrol.2021.126386
- 15. Issayeva A., Abubakirova A., Syzdykova M., Arystanova S., Anlamasova G., Zhumakhanova R., Leska B. 2022. Fe₂(SO₄)₃ and Bentonite Use to Reduce COD Indicators in Wastewater Containing Detergents. Journal of Ecological Engineering, 23(3), 68–73.
- 16. Khera R., Ransom P., Guttridge M., Speth T.F. 2021. Estimatingcostsfornitrateandperchloratetreatmen tforsmalldrinkingwatersystems. AWWA WatSci, 3(2), e1224. https://doi.org/10.1002/aws2.1224
- Kim Y.N., Kim M.Y., Choi M. 2016. Synergistic integration of catalysis and ion exchange for highly selective reduction of nitrate into N2. Chemical Engineering Journal, 289, 423–432. (Multi-Language)

- Kirisits M.J., Emelko M.B., Pinto A.J. 2019. Applying biotechnology for drinking water biofiltration: advancing science and practice. Current opinion in biotechnology, 57, 197–204. https://doi. org/10.1016/j.copbio.2019.05.009
- Lee M.S., Lee K.K., Hyun Y., Clement T.P., Hamilton D. 2006. Nitrogen transformation and transport modeling in groundwater aquifers. Ecological Modelling, 192(1), 143–159. https://doi. org/10.1016/j.ecolmodel.2005.07.013
- 20. Lin Y.H., Gu Y.J. 2020. Denitrification Kinetics of Nitrate by a Heterotrophic Culture in Batch and Fixed-Biofilm Reactors. Processes, 8(5), 547. https://doi.org/10.3390/pr8050547
- 21. Marchesini F., Mendow G., Picard N., Zoppas F., Aghemo V., Gutierrez L., Querini C., Miró E. 2019. PdInCatalystsin a Continuous Fixed Bed Reactor fo rthe Nitrate Removal from Ground water. International Journal of Chemical Reactor Engineering, 17(6), 20180126. https://doi.org/10.1515/ijcre-2018-0126
- 22. Martínezde Zabarte Fernández J.M, García Íñiguez J.P., Domínguez Cajal M. 2018. Metahemoglobinemia enlactantes mayores de unaño. Medicina Clínica (English Edition), 151(7), 278–280. https:// doi.org/10.1016/j.medcle.2017.12.037
- 23. Matei A., Racoviteanu G. 2021. Review of the technologies for nitrates removal from water intended for human consumption. IOP Conference Series: Earth and Environmental Science, 664, 012024. https://doi.org/10.1088/1755-1315/664/1/012024
- 24. Mohseni-Bandpi A., Elliott D.J., Zazouli M.A. 2013. Biological nitrate removal processes from drinking water supply-a review. Journal of environmental health science & engineering, 11(1), 35. https://doi.org/10.1186/2052-336X-11-35
- 25. Pirsaheb M., Khosravi T., Sharafi K., Mouradi M. 2016 Comparing operational cost and performance evaluation of electrodialysis and reverse osmosis systems in nitrate removal from drinking water in Golshahr, Mashhad. Desalination and Water Treatment, 57(12), 5391–539. https://doi.org/10.1080/1 9443994.2015.1004592
- 26. Richards J., Chambers T., Hales S., Joy M., Radu T., Woodward A., Humphrey A., Randal E., Baker M.G. 2022. Nitrate contamination in drinking water and colorectal cancer: Exposure assessment and estimated health burden in New Zealand. Environmental Research, 204(C), 112322. https://doi. org/10.1016/j.envres.2021.112322
- 27. Rocher V., Mailler R., Mèche P., Pichon S., Bernier J., Guérin S., Ferro O., Augé A., Boursaud L., Bord G., Bulteau J., Azimi S. 2019. Clogging limitation of nitrifying biofilters: BiostyrDuo® process study. Water Practice and Technology, 14(1), 43–54. https://doi.org/10.2166/wpt.2018.107

- 28. Rodríguez-Escales P., Folch A., Van Breukelen B., Vidal-Gavilán G., Sanchez-Vila X. 2016. Modeling long term Enhanced in situ Biodenitrification and induced heterogeneity in column experiments under different feeding strategies. Journal of hydrology, 538, 127–137. https://doi.org/10.1016/j. jhydrol.2016.04.012
- 29. Roshanravan H., Borghei M., Hassani A.H., Vagheei R. 2021. Nitrate removal from drinking water wells by heterotrophic denitrification using citric acid as a carbon source and ozonation. Journal of Water and Wastewater, 31(7), 63–77. (in Persian) https://doi.org/10.22093/wwj.2020.201484.2928
- Ruiz-Bevia F., Fernandez-Torres M.J. 2019. Effective catalytic removal of nitrates from drinking water: An unresolved problem? Journal of Cleaner Production, 217, 398–408. https://doi.org/10.1016/j.jclepro.2019.01.261
- 31. Sharma S., Bhattacharya A. 2017. Drinking water contamination and treatment techniques. Appl Water Sci, 7, 1043–1067. https://doi.org/10.1007/ s13201-016-0455-7
- 32. Sherris A.R., Baiocchi M., Fendorf S., Luby S.P., Yang W., Shaw G.M. 2021. Nitrate in Drinking Water during Pregnancy and Spontaneous Preterm Birth: A Retrospective Within-Mother Analysis in California. Environ Health Perspect, 129(5), 57001. https://doi.org/10.1289/EHP8205
- 33. Shrestha S., Semkuyu D.J., Pandey V.P. 2016. Assessment of groundwater vulnerability and risk to pollution in Kathmandu Valley, Nepal. The Science of the total environment, 556, 23–35. https://doi.org/10.1016/j.scitotenv.2016.03.021
- 34. Simonič M., Andreja Goršek A., Petrovič A. 2017. Nitrate Removal from Groundwater with Membrane Bioreactor, Nitrification and Denitrification, Ivan X. Zhu, IntechOpen, https://doi.org/10.5772/ intechopen.68718.
- 35. Taneja P., Labhasetwar P., Nagarnaik P., Ensink J. 2017. The risk of cancer as a result of elevated levels of nitrate in drinking water and vegetables in Central India. Journal of water and health, 15(4), 602–614. https://doi.org/10.2166/wh.2017.283
- 36. Tokazhanov G., Ramazanova E., Hamid S., Bae S., Lee W. 2020. Advancesinthecatalyticreductio nofnitratebymetalliccatalystsforhighefficiencyand N2 selectivity: A review. Chemical Engineering Journal, 384, 123252. https://doi.org/10.1016/j. cej.2019.123252
- 37. Ward M.H., Jones R.R., Brender J.D., de Kok T.M., Weyer P.J., Nolan B.T., Villanueva C. M., van Breda S.G. 2018. Drinking Water Nitrate and Human Health: An Updated Review. International journal of environmental research and public health, 15(7), 1557. https://doi.org/10.3390/ijerph15071557