UDC 631.461.4; 631.461.71; 66.067.9
DOI: 10.24025/2306-4412.3.2023.278907

MATHEMATICAL MODEL OF THE ASSOCIATED PROCESSES OF DENITRIFICATION AND RENEWAL OF SULFATES IN AN INNOVATIVE BIOFILTER

Ivan Borysov
PhD Student
Ukrainian State University of Chemical Technology
Gagarin Ave., 8, Dnipro, 49005, Ukraine
https://orcid.org/0000-0003-0982-245X
Viktor Gevod
Doctor of Chemical Sciences, Associate Professor
Ukrainian State University of Chemical Technology
Gagarin Ave., 8, Dnipro, 49005, Ukraine
https://orcid.org/0000-0002-5027-6916
e-mail: aquilegya@ua.fm

Abstract. The problem of pollution of underground water sources with nitrates, as well as geogenic compounds (sulfates, hydrocarbonates) is of interest to researchers around the world. Nitrates represent a particular risk to the health of the population living in places without centralized water treatment. In this case, post-treatment of water at the point of use is recommended using both technologies for the removal of nitrates from treated water and their biological conversion into nitrogen. Without downplaying the role of the former, the latter technologies are seen as promising, requiring research and improvement.

The purpose of the work is to study the process of nitrate biotransformation in a small submersible biofilter in the presence of basic groundwater anions (sulfates and hydrocarbonates) and their effect on the quality of treated water. The shift of sulfate-sulfide balance in aquatic environment of the biofilter and the influence of the concentrations of sulfate ions and the substrate of bacterial nutrition on the accumulation of hydrogen sulfide and its consumption in the volume of the biofilter have been studied. It is shown that the processes of denitrification and reduction of sulfates to hydrogen sulfide proceed sequentially. The reduction of sulfates to hydrogen sulfide begins after the removal of nitrates from the treated water at a dosage of the nutrient substrate that exceeds the stoichiometric requirement for denitrification. Hydrogen sulfide, which is formed in the zone of connection of inlet and outlet knees of the biofilter, is practically not detected at its outlet. The reduction of sulfates associated with the removal of nitrates can be a useful tool for additional treatment of water from impurities of heavy and polyvalent metal ions.

Keywords: decentralized water treatment, nitrates, hydrogen sulfide, bacterial nutrition, water quality.

Introduction

The growth of the population and the demand for food contribute to the intensification of agriculture, in particular, through the use of fertilizers based on both organic and inorganic compounds of nitrogen. This is one of the main causes of groundwater pollution with nitrates. According to estimates (Matei *et al*., 2021; Benes *et al*., 1989), only 40-60% of the total amount of nitrate fertilizers applied to the soil is consumed by plants, the latter in the form of nitrate ions (NO_3^-) entering water sources (soil and underground), which leads to their contamination.

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Nitrate ions are a stable form of bound nitrogen, poorly sorbed by water-bearing soils, capable of migrating over aquifers over long distances, penetrating deep-lying strata, which leads to permanent nitrate pollution (Besser *et al*., 2022) of underground water sources. This limits their use for domestic and drinking water supply due to serious risks to human health, and also provokes a number of environmental problems.

Literature review

The main danger of nitrates entering the human body is associated with the occurrence of methemoglobinemia in young children (Fewtrell, 2004). Based on this, WHO recommended a limit of nitrate content in drinking water of ≤50 mg/dm^3 in the form of (NO_3^-) . However, the consequences for human health, the appearance of which is likely at lower concentrations of nitrate ions in water and may be associated with the immunosuppressive effect of nitrates, a decrease in the body's resistance to the action of mutagenic and carcinogenic agents, malignant tumors, reproductive risks, etc., continue to be studied (Ward *et al*., 2018; Noori *et al.*, 2022; Temkin *et al*., 2019; Grout *et al*., 2023).

The concentration of nitrates in groundwater is affected by climate change (Sidiropoulos *et al*., 2019; Paradis *et al*., 2016). Its growth is predicted as a result of a decrease in groundwater level due to the degradation of water resources (a decrease in the amount of groundwater in the future water balance). Despite the adopted legislation (Nitrate Directive, 1991/676/EEC; Water Framework Directive, 2000/60/EEC), nitrate pollution of groundwater in the world (Abascal *et al*., 2022) is a global problem, which is also inherent in Ukraine (Romanchuk *et al.*, 2021; Herasymchuk *et al*., 2022). The work (Romanchuk *et al.*, 2021) shows that in 10 out of 15 studied regions of Ukraine, the nitrate content in drinking well water in rural settlements was exceeded both during traditional and organic farming. According to (Natsionalna dopovid, 2022), only 23.5% of Ukrainian villages are provided with centralized water supply. The rest of the population of rural residential areas uses drinking water from wells, boreholes, catchments. From 14.2% to 45.6% (depending on the type of source) of drinking water samples did not meet the standards (DSanPiN, n.d.) for sanitary and chemical indicators, including nitrate content from 13.4 to 36.3%. There are cases when this indicator reached 63.9% (Herasymchuk *et al*., 2022). The use of such water for drinking is possible only after its purification. In places where there are no centralized drinking water treatment sites and water distribution networks, to reduce high levels of concentrations of nitrate and other harmful impurities, it is recommended to use water purification devices at points-of-use (POU) and at points-of-entry (POE). Most often, reverse osmosis and ion exchange devices are used. Their advantages and disadvantages are described in (Matei *et al*., 2021; Jensen *et al.*, 2021). High investment and operating costs are a deterrent to the use of such devices in regions with low population incomes (Grout *et al*., 2023). The use of biofiltration can be an alternative.

The study (Alguacil-Duarte *et al*., 2022) of life cycle assessment (LCA) and economic efficiency analysis of two processes of drinking water treatment (reverse osmosis and biological purification) has shown that biological technology allows to produce drinking water in a more *environmentally* safe, *economical* and *efficient* way.

Currently, slow sand filters (SSF) and biological sand filters (BSF) are increasingly being considered as one of the available alternatives to POU. Recently published reviews (Freitas *et al.*, 2022; Maiyo *et al*., 2023) note that these filters were originally focused on removal of silted particles, turbidity, color, and pathogenic microorganisms. However, thanks to the improvement of the design, construction of filter loads, water purification modes, the capabilities of biofilters have been significantly expanded, including for nitrate removal

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(Romero *et al*., 2020; Mutsvangwa *et al*., 2017; Aslan *et al*., 2007; Mohobane *et al*., 2022; Roshanravan *et al*., 2021).

At the same time, the control over microbiological processes taking place and the management of clogging (clogging) of the filter layer remain the weak point of biological filtration (Rocher *et al*., 2019). As an alternative to the existing POU biofilters, the concept of a biofilter with minimal additional maintena (Gevod *et al*., 2021), resistance to clogging of its filter layer was evaluated. The latter consisted of elements of a certain size and configuration with a highly developed surface and colonies of heterotrophic denitrifying bacteria attached to it. Loading elements ensured the creation of channels in the filter layer for unhindered movement of denitrified water along the path of biofiltration and the release of gaseous products of microbial metabolism, in particular molecular nitrogen, from the biofilter into atmospheric air. The change of filtration mode from continuous direct flow to piston (displacement) minimized the formation of excess biomass entering the filtrate.

However, in addition to nitrates, groundwater also contains other inorganic compounds (salts of heavy and polyvalent metals, carbonates, sulfates, etc.), which take part in associated processes (methanogenesis, sulfate reduction, ureolysis) in the biofilter. Therefore, the study of these processes that can affect the quality of treated water is relevant.

The purpose of the study was to reveal additional possibilities of denitrification small-sized, submersible biofilter, namely, biotransformation together with nitrates of sulfates to hydrogen sulfide, which can contribute to the removal of ions of heavy and polyvalent metals from water.

It is known that the increased content of nitrates suppresses the activity of sulfate-reducing bacteria (He *et al*., 2010) in the immobilization of heavy and polyvalent metal ions in the form of insoluble sulfides and oxides.

The object of research was a shift in the sulfate-sulfide balance in aqueous environment of the biofilter and the influence of concentrations of sulfate ions and the substrate of bacterial nutrition, in particular ethanol, on the accumulation of H_2S and its consumption in the biofilter volume during biofiltration denitrification.

Experimental part. Materials and methods

The microbiological reduction of sulfates to hydrogen sulfide H_2S with its subsequent transformation into colloidal sulfur in the process of denitrification of water in a biofilter operating in displacement (piston) mode was studied. The design of the biofilter, the type of filter load, and the mode of incubation of biofoulings were described in detail in (Gevod *et al*., 2021). Samples of purified water were taken for analysis (Fig. 1) from inlet zone (1) of inlet elbow, outlet zone (3) of outlet elbow, and from connection zone (2) of inlet and outlet elbows. The sample volume from each sampling point was 150 ml. During the research, 5 liters of water for denitrification were supplied to the biofilter in a "volley" at a given time every day, and the same amount of filtrate (denitrified water) was simultaneously received. Time of hydraulic water retention in the biofilter was determined by its volume supplied to biofiltration, the length of the filtration path, did not depend on other parameters of the process and was two and a half days, which exceeded the necessary time for exhaustive denitrification of water.

Model solutions of nitrate water were used in the work. They were prepared on the basis of tap water containing sulfates (125 mg/dm^3) by adding ($NaNO_3$) to it. The concentration of the latter was 250 mg/dm^3. In separate experiments, distilled water was used to prepare sulfate-free nitrate water. Ethyl alcohol (C_2H_5OH) was used as a nutrient substrate. Its

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concentration during the research was 60 mg/dm^3 and 125 mg/dm^3. The choice of the type of nutrient substrate was determined by the target (drinking) purpose of the treated water and existing recommendations in the literature (Mutsvangwa *et al*., 2017; Mohseni-Bandpi *et al*., 2013).

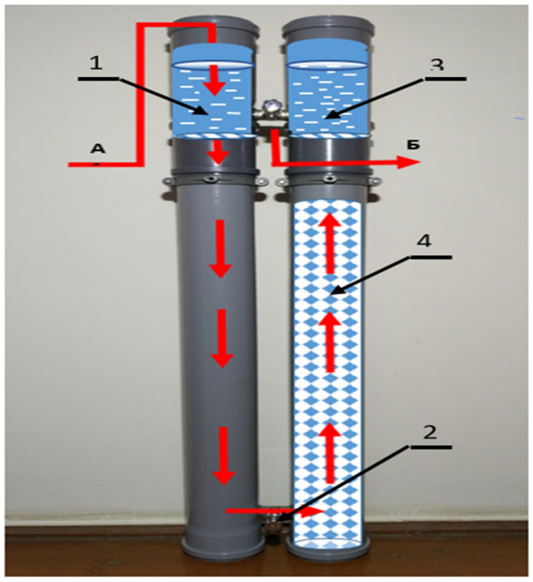

Figure 1. General view of the biofilter with a cross-section of its outlet elbow and the positions of sampling sites for analyzes:
1 - inlet zone; 2 - zone of connection of inlet and outlet elbows; 3 - output zone of outlet elbow; 4 - biofilter loading: A-B – direction of water movement through the biofilter

The concentration of nitrates in water was measured by I-160 MI ionometer with ELIS-121NO3 ion-selective electrode and EVL1-M reference electrode. The working range of nitrate ion concentration measurements was 10^{-1}-5.10^{-5} M. The sensitivity was 5×10^{-6} M.

The concentration of ethanol in water samples from 1-3 zones of the biofilter was determined using GC9790 III gas chromatograph with flame ionization detector and short packed column (diameter is 3 mm, length is 500 mm). Chromosorb W treated with polyethylene glycol (PEG 20M) was the packing material. The temperatures of the ejector, detector, and column were kept constant and were, respectively, 160°C, 200°C, and 120°C. Molecular nitrogen (N_2) of 99.995 qualification was the mobile phase. The dosage of liquid samples into the ejector liner was equal to 0.2 µl and 0.1 µl. Samples were entered manually. A microsyringe with a volume of 1 µl was used. Processing of chromatograms was carried out automatically according to the algorithms of "FL9790 chromatogram Workstation" software.

The appearance and consumption of hydrogen sulfide in the connection zone of inlet and outlet elbows were monitored based on the results of measurements of the value of redox potential (Eh). For this purpose, ERP-101 measuring electrode and EVL1-M silver chloride reference electrode, which were connected to I-160MI ionometer, and also - by the reaction of qualitative determination of hydrogen sulfide using a solution of $[Pb(NO_3)_2]$ lead nitrate and by characteristic smell of water sample, were used. In the cells of the potentiometer, selected water samples from three zones of the biofilter were mixed with magnetic stirrers at a speed of 120 rpm and atmospheric air was freely accessible to them. The area of the sample mirror was 0.2 dm^2. When measuring (Eh), the electrode pair, pre-exposed in tap water with an equilibrium concentration of dissolved oxygen in it, was moved into the cell with the test sample and potentiometer readings were taken after 5 minutes of exposure time.

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pH control was carried out with I-160MI ionometer with ESK 10603 pH glass electrode and EVL1-M silver chloride reference electrode. Concentrations of nitrate ions, Eh and pH were measured and recorded automatically according to a given algorithm using the "Analytics" software.

Results and discussion

During denitrification, the reduction of sulfates manifests itself in that part of the filter load, where the biofiltered water contains a sufficient amount of dissolved sulfates and bacterial nutrients (donors of assimilated carbon and electrons), but has practically no dissolved oxygen. Under anaerobic conditions, sulfate-reducing bacteria split oxygen from (SO_4^{2-}) sulfate ions and produce (HS^-) hydrosulfide ions. The latter undergo hydrolysis and hydrogen sulfide is formed in water. Its presence in water samples is revealed by a qualitative reaction using [$Pb(NO_3)_2$] and by the results of redox potential (Eh) measurements.

Natural water that does not contain hydrogen sulfide, at neutral, weakly acidic and weakly alkaline pH values, is characterized by redox potentials (Eh) in the range from plus 50 mV to plus 300 mV on the hydrogen scale (Piskarev *et al*., 2010). Eh value depends on the content of dissolved mineral and organic impurities with different degrees of oxidation in water. Positive values of redox potentials are determined in water by impurities in an oxidized state. The appearance of hydrogen sulfide, which is a strong reducing agent, shifts the redox potential of water in negative direction to values in the range from minus 250 mV to minus 300 mV.

Fig. 2 shows measured concentrations of nitrate ions, Eh, and pH in the samples taken for analysis from positions 1, 2, and 3 (Fig. 1) before supplying another new portion of water for biofiltration. It was supplied daily (stationary mode of functioning of the biofilter) at a given time. The output water contained 250 mg/dm^3 of sodium nitrate, 125 mg/dm^3 of sulfates, and 125 mg/dm^3 of ethanol (carbon/nitrogen ratio C/N = 1.56), which is excessive compared to the stoichiometry of biological denitrification (28) when C/N = 0.94. Columns of different heights in sector (a) in Fig. 2 show nitrate concentrations in water samples that have been taken for research at the biofilter inlet (position 1), from the sampler at the junction of inlet and outlet elbows of the biofilter (position 2) and at the biofilter outlet (position 3). As can be seen, during the operation of the biofilter in the displacement biofiltration mode, a multiple (by more than an order of magnitude) reduction in the concentration of nitrate ions in denitrified water is achieved. At the same time, the main share of the observed decrease in the concentration of nitrate ions falls on the inlet elbow of the biofilter. In sectors (b) and (c) of the diagram field, the results of Eh and pH measurements are presented. In the water supplied to the biofilter and in the resulting filtrate, redox potentials have positive values, which on the hydrogen scale range from plus 90 mV to plus 135 mV. In the water sampled for analysis from the connection zone of inlet and outlet elbows of the biofilter, Eh have negative values, which vary in the range from minus 230 mV to minus 265 mV.

The hydrogen index (pH) of the water supplied to the biofilter and in the obtained biofiltrate is in the range of 8.1-8.3 and 8.45-8.7, respectively, and in the sample from the zone of connection of inlet and outlet elbows - 7.6-7.8.

The results of Eh measurements indicate the presence of hydrogen sulfide in the zone of connection of inlet and outlet elbows of the biofilter. Samples of denitrified water from this zone have a characteristic odor. The presence of hydrogen sulfide in them is confirmed by a qualitative reaction using lead nitrate.

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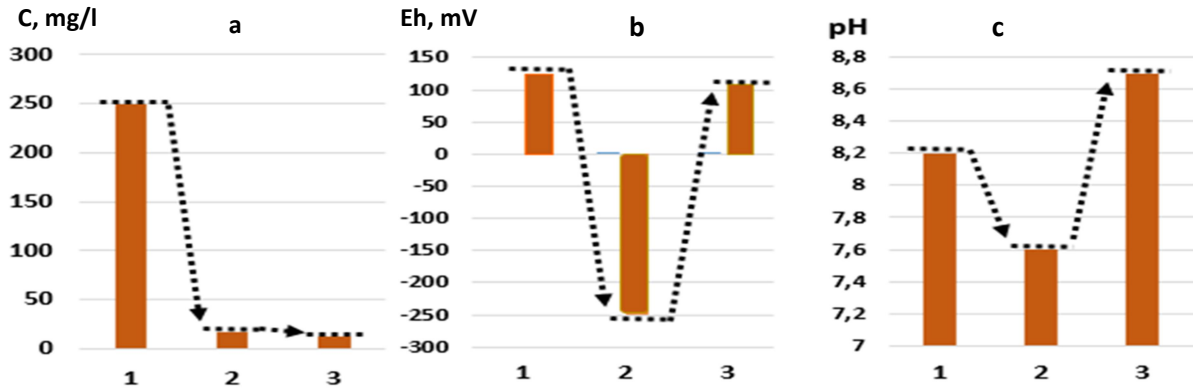

Figure 2. Change in nitrate concentration (a), redox potential (b), and pH (c) in water samples:
1 - inlet zone; 2 - zone of connection of inlet and outlet elbows; 3 - output zone of outlet elbow

Thus, during biofiltration denitrification of water with ($NaNO_3$) initial concentration – 250 mg/dm^3, sulfate concentration – 125 mg/dm^3 and ethanol dosage – 125 mg/dm^3, in the lower part of the biofilter (anaerobic zone) the presence of sulfate-reducing bacteria is observed. The latter separate oxygen from sulfate ions for their respiration and release (HS^-) hydrosulfide ions that undergo hydrolysis into the filtered water, which is accompanied by the appearance of hydrogen sulfide in denitrified water along the path of biofiltration.

Between hydrosulfide ions and hydrogen sulfide molecules, a dissociation equilibrium is established, and between sulfate ions, hydrosulfide ions, and hydrogen sulfide, a redox equilibrium, associated with the functioning of sulfate reductases in bacterial cells that reduce (SO_4^{2-}) ions to (HS^-), is established.

The ($H_2S \rightleftarrows HS^-$) dissociation equilibrium depends on pH and the ionic strength formed by salts dissolved in water. If the ionic strength is neglected, then the equilibrium between (HS^-) and (H_2S)) depends only on pH and is described by the equation:

$$H_2S \rightleftarrows H^+ + HS^-. \quad (1)$$

For this reaction, the standard Gibbs potential ($\Delta G°_{298}$) is:

$$\Delta G°_{298} = 40.27 \text{ kJ/mol}. \quad (2)$$

The ratio of the standard Gibbs potential ($\Delta G°_{298}$) to the energy of thermal motion (RT) is the logarithm of the dissociation equilibrium constant, i.e.:

$$\lg K = \frac{-\Delta G^0_{298}}{2.303RT}. \quad (3)$$

So, in this way:

$$\lg K = -7.05; \text{ and } K = 8.91 \cdot 10^{-8}, \quad (4)$$

however

$$K = \frac{[H^+][HS^-]}{H_2S}, \quad (5)$$

and

$$lg\frac{[HS^-]}{[H_2S]} = lgK + pH. \quad (6)$$

Equation (6) reveals the relationship between pH and the concentration ratio of hydrosulfide ions to hydrogen sulfide in their presence in water. In particular, if $[H_2S] = [HS^-]$, then:

$$\lg K + pH = 0, \text{ and } pH = 7.05. \quad (7)$$

If pH < 7.05, the hydrogen sulfide equilibrium according to reaction (1) shifts to $[H_2S]$, and when pH > 7.05 - to $[HS^-]$.

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Concentrations of hydrogen sulfide and hydrosulfide ions at different pH values are found as follows:

$$K_1 = \frac{[H_2S][OH^-][H^+]}{[HS^-][H^+]} = \frac{K_W}{K} = \frac{\alpha^2[HS^-]^2}{(1-\alpha)[HS^-]}, \quad (8)$$

where: K_W is ionic product of water; K_1 is a constant of H_2S dissociation reaction according to the first degree; α^* is a degree of hydrolysis of hydrosulfide ions; $[HS^-](1-\alpha^*)$ is a concentration of hydrosulfide ions that have not undergone hydrolysis; $\alpha^*[HS^-]$ is a concentration of formed (H_2S) and (OH^-).

Then:

$$[HS^-] = \frac{[OH^-]^2}{K_1} = \frac{10^{-2(14-pH)}}{K_1} \quad (9)$$

or

$$[H_2S] = \alpha[HS^-] = \sqrt{K_1[HS^-]}. \quad (10)$$

If sulfate ions are present in water together with hydrogen sulfide and hydrosulfide ions, then the situation changes. In sulfate ions, sulfur has a (+6) oxidation state, and (-2) in hydrogen sulfide molecules and hydrosulfide ions. The equilibrium in water between (SO_4^{2-}) and (HS^-) ions, as well as between (SO_4^{2-}) and (H_2S) ions depends on both pH, as well as energy expenditure required for the reduction of sulfate ions. Sulfate-reducing bacteria obtain energy for the work of enzyme complexes that split oxygen from (SO_4^{2-}) ions and produce (H_2S) ions from nutrient substrates.

The recovery of (SO_4^{2-}) to (H_2S) is described by the equation:

$$SO_4^{2-} + 10H^+ + 8e = H_2S + 4H_2O. \quad (11)$$

The standard Gibbs potential for this reaction is equal to:

$$-\Delta G^\circ_{298} = 233.91 \text{ kJ/mol}, \quad (12)$$

and, thus, the standard redox potential is described by the expression:

$$Eh^0 = \frac{-\Delta G^0_{298}}{8F}. \quad (13)$$

Then, according to the Nernst equation, the relationship between $[SO_4^{2-}]$ and $[H_2S]$ concentrations with redox potential and pH is as follows:

$$Eh = Eh^0 - \frac{2.3R}{nF} lg \frac{[H_2S]}{[SO_4^{2-}]} - \frac{2.3RT}{F}\frac{(n_H)}{(n_e)}pH \quad (14)$$

or

$$Eh = 0.303 + 0.0074 lg \frac{[SO_4^-]}{[H_2S]} - 0.074pH \quad (15)$$

and

$$lg \frac{[SO_4^{2-}]}{[H_2S]} = \frac{Eh - 0{,}303 + 0{,}074pH}{0{,}0074} = Q. \quad (16)$$

Assuming that

$$[H_2S] + [SO_4^{2-}] = const,$$

and imagining the concentrations of indicated components as fractions from the unit, we get:

$$[SO_4^{-2}]^* + [H_2S]^* = 1 \quad (17)$$

or

$$[SO_4^{-2}]^* = \frac{10^Q}{1+10^Q} \quad (18)$$

and

$$[H_2S]^* = \frac{1}{1+10^Q}. \quad (19)$$

The equilibria between $[SO_4^{2-}]$ and $[HS^-]$ can be described in a similar way, i.e.:

$$SO_4^{2-} + 9H^+ + 8e = HS^- + 4H_2O, \quad (20)$$

$$-\Delta G^\circ_{298} = 194.54 \text{ kJ/mol}, \quad (21)$$

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$$Eh^0 = \frac{-\Delta G^0_{298}}{8F} = 0.252 \text{ V}, \quad (22)$$

$$Eh = Eh^0 - \frac{2.3RT}{nF} lg \frac{[HS^-]}{[SO_4^{2-}]} - \frac{2.3R}{F} \frac{(n_H)}{(n_e)} pH \quad (23)$$

and

$$Eh = 0.252 + 0.0074 lg \frac{[SO_4^{2-}]}{[HS^-]} - 0.066pH. \quad (24)$$

Then:

$$lg \frac{[SO_4^{2-}]}{[HS^-]} = \frac{Eh-0{,}252+0{,}066pH}{0{,}0074} = Q_1 \quad (25)$$

and by analogy with (17)-(19):

$$[SO_4^{-2}]^* = \frac{10^{Q_1}}{1+10^{Q_1}}, \quad (26)$$

$$[HS^-]^* = \frac{1}{1+10^{Q_1}}. \quad (27)$$

Equation (9) indicates that in a hydrogen sulfide system, a shift in pH by one unit causes a change in the concentration of hydrosulfide ions by two orders of magnitude. At the same time, the concentration of hydrogen sulfide also changes proportionally, as follows from equation (10).

Fig. 3A shows how relative concentrations of sulfate ions and hydrosulfide ions change depending on pH at redox potentials equal to 0.2 V; 0.25 V and 0.3 V, respectively, and Fig. 3B - how decimal logarithms of the ratio of concentrations of sulfate ions to hydrosulfide ions change depending on the values of redox potentials at pH = 6.6; 7.6 and 8.6.

The ratios of concentrations of sulfate ions to hydrosulfide ions, depending on redox potentials, are exponential functions. In semi-logarithmic coordinates, their graphs are straight lines with a slope: $nF/2.3RT$. Their location occurs with a displacement along the ordinate axis proportional to pH, as shown by equations (23)-(25). At a given pH value, an increase or decrease in redox potential by 0.01 V leads to a change in the concentration ratio more than twenty times. Therefore, the processes occur most dynamically in the hydrogen sulfide system near the points of concentrations equality $[SO_4^{2-}]$ and $[HS^-]$, or $[SO_4^{2-}]$ and $[H_2S]$. This is illustrated in Fig. 3A. On it, black dashed curves 1*, 2*, 3* demonstrate how the concentration of sulfate ions can change at redox potentials equal to minus 0.2 V; minus 0.25 V; and minus 0.3 V, when the hydrogen index increases from 6.5 to 7.0, respectively; also from 7.5 to 8.0 and from 8.0 to 8.5. Red continuous lines show, at the same time, the change in relative concentrations of hydrosulfide ions. Calculations have been made according to equations (26) and (27) using the values obtained in (25). It can be seen that an increase in the hydrogen index by 0.5 units leads to a change in relative concentrations of $[SO_4^{2-}]$ and $[HS^-]$ from almost zero to one and vice versa.

The course of calculated curves 2 and 2* in Fig. 3A corresponds to the results of experimental measurements, which have shown a shift of redox potential to minus 260 mV and pH to 7.6 (Fig. 2b, c). Their intersection occurs at pH 7.6-7.62, which corresponds to the possibility of achieving the same relative concentrations of hydrosulfide ions and sulfate ions at Eh = 0.25 V. In fact, the concentration of hydrosulfide ions produced by sulfate-reducing bacteria is related to the amount and quality of the substrate for their nutrition. In denitrification biofilter, ethanol, part of which from denitrification zone, under conditions of excess, enters sulfate reduction zone, is such a substrate of bacterial nutrition. Therefore, real concentrations of hydrosulfide ions and, accordingly, hydrogen sulfide, compared to the initial amount of sulfate ions in water fed to the biofilter for processing, are not large.

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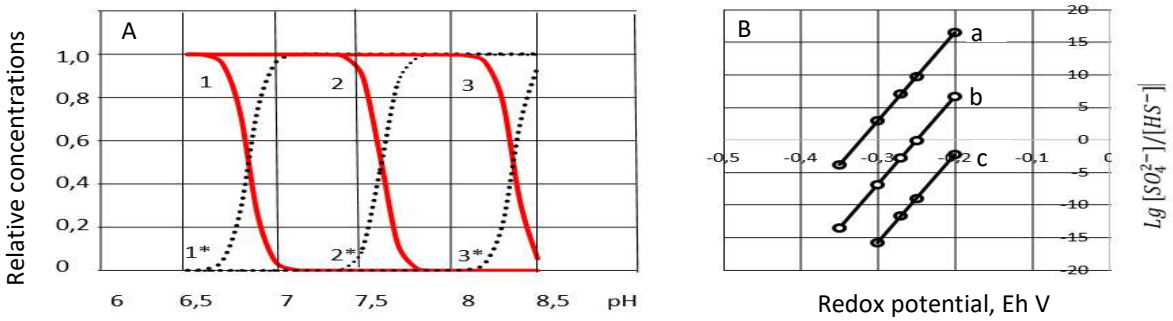

Figure 3. Calculated dependences of relative concentrations of hydrosulfide ions and sulfate ions and decimal logarithms of their ratios depending on pH at given Eh:
A - 1, 2, 3 - change in relative concentrations of hydrosulfide ions and 1*, 2*, 3* - sulfate ions depending on pH at Eh = -0.2 V; -0.25 V; -0.3 V respectively
B - $\lg[SO_4^{2-}]/[HS^-]$ on Eh at pH=6.6 (a); 7.6 (b); 8.6 (c)

Fig. 4 shows the dependence of the change of redox potentials (Eh) on time in water samples taken for analysis from zones of: a) inlet elbow; b) connection of inlet and outlet elbows of the biofilter; c) outlet elbow of the biofilter. Measurements of redox potentials were carried out in samples that were in states of rest (1), stirring with magnetic stirrer (2), as well as mixing a stream of air bubbles (3) with additional blowing through the sample of filtered water.

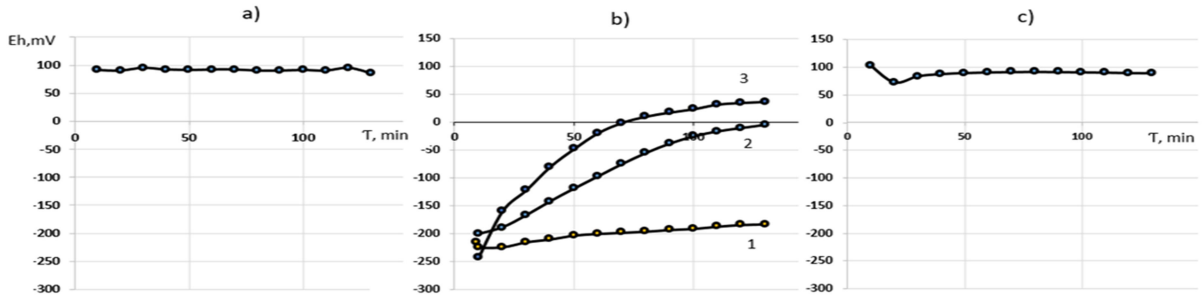

Figure 4. Dynamics of changes in redox potentials in water samples taken for analysis from different zones of the biofilter:
a) zone of inlet elbow; b) zone of connection of inlet and outlet elbows;
c) zone of outlet elbow of the biofilter

The graphs of the "Eh - τ" function in Fig. 4 show that Eh in samples of water entering biofiltration (a) and in the obtained biofiltrate (c) practically do not differ from each other and are stable over time. Therefore, the conditions of the experiment (state of rest or mixing of water samples with magnetic stirrer) do not have a noticeable effect on Eh indicators. Such dynamics of changes in redox potentials over time indicates the absence of significant amounts of reduced sulfur compounds, in particular hydrosulfide ions and hydrogen sulfide, in water entering biofiltration and in denitrified water. On the other hand, a different picture is observed in biofiltrate samples obtained from the zone of connection of inlet and outlet elbows of the biofilter (b). The course of changes in the "Eh - τ" functions in these samples is significantly influenced by hydrodynamic conditions. If water sample in the measuring cell of the potentiometer is at rest (magnetic stirrer is turned off), redox potential during its measurement changes as shown by curve 1 (sector b). When water sample is mixed with

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magnetic stirrer, redox potential changes as shown by curve 2. Under the conditions of blowing the water sample with a stream of air bubbles in addition to mixing, effective surface area of water-air phase separation in the measuring cell increases significantly and the change in Eh values is demonstrated by curve 3.

The results of this experiment testify to the process of sulfate reduction with the formation of H_2S. During the contact of filtrate samples containing hydrogen sulfide with atmospheric air, hydrogen sulfide is weathered. The difference in its concentrations (partial pressures) in the sample volume and in atmospheric air is the driving force. The process is accelerated by convective transfer of dissolved hydrogen sulfide to the surface of "water-air" phase interface during mixing and additional blowing of the samples with atmospheric air.

From the obtained data, it is possible to conclude that during the daily supply of portions of nitrate water of the above composition to the biofilter the formation of hydrogen sulfide is observed in the zone of connection of its inlet and outlet elbows. Its appearance is caused by the fact that the dosage of ethanol in denitrified water, which is 125 mg/dm^3, exceeds the stoichiometric one (C/N = 0.94), calculated by the equation:

$$NO_3^- + 0{,}55C_2H_5OH + 0.137O_2 \rightarrow 0{,}046C_5H_7O_2N + 0{,}87HCO_3^- + 0{,}99H_2O + \\ + 0{,}13OH^- + 0{,}48N_2. \quad (28)$$

Due to the biotransformation of nitrates into molecular nitrogen in the presence of ethanol, the concentration of nitrate ions in the filtrate decreases. This contributes to the activation of sulfate-reducing bacteria (He *et al*., 2010), which are localized in the zone of connection of inlet and outlet elbows of the biofilter. In the presence of ethanol, they produce hydrogen sulfide, releasing oxygen from sulfate ions for their respiration. The equation of bacterial sulfate reduction looks like this:

$$3SO_4^{2-} + 2CH_3CH_2OH = 3HS^- + 3H_2O + CO_2 + 3\,HCO_3^-. \quad (29)$$

Hydrogen sulfide, which is formed in the zone of connection of inlet and outlet elbows of the biofilter, is practically not observed at its outlet. It can be assumed that in the filter loading after the zone of operation of sulfate-reducing bacteria, there is a zone of prevalence of sulfur bacteria that oxidize hydrogen sulfide, which hasn't been spent on the formation of insoluble sulfides, to elemental sulfur.

Sulfate reduction is suppressed if the addition of ethanol to denitrified water is less (60 mg/dm^3, i.e. C/N = 0.75) than is required for exhaustive microbiological reduction of nitrate to molecular nitrogen according to equation (28).

Fig. 5 shows "Eh - τ" chronopotentiograms of filtrate samples taken for analysis from zone (2) of the biofilter during the decade of the experiment. The course of obtained "Eh - τ" dependences, as expected, confirms that with a decrease in the dosage of ethanol in denitrified water, sulfate-reducing bacteria stop producing hydrogen sulfide. Its accumulation in the biofiltrate decreases as the period of "starvation" of the microbial community increases, and already after five days of the biofilter's work, under certain conditions, the chronopotentiograms record the disappearance of hydrogen sulfide. This is demonstrated by the general course of the curves with indices from 0 to 5 in Fig. 5a. However, if ethanol dosage is restored to the original value of 125 mg/dm^3, then the picture is reversed. In working biofilter, the production of hydrogen sulfide is resumed in the zone of connection of its inlet and outlet elbows. This demonstrates the course of "Eh - τ" curves with indices from 5 to 10 in Fig. 5b.

DOI: 10.24025/2306-4412.3.2023.278907

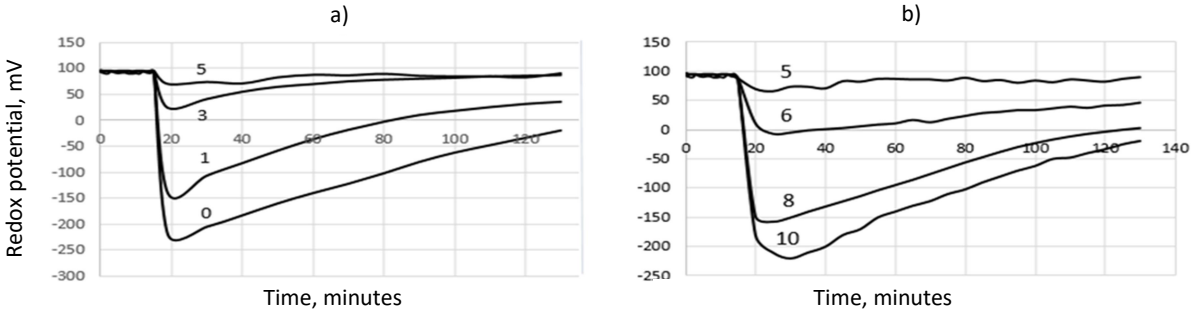

Figure 5. Dynamics of the change in redox potentials during 10 days in biofiltrate samples stirred with magnetic stirrer at different doses of ethanol:
a) curve 0 - dose of ethanol is 125 mg/dm^3; curves 1, 3, 5 - dose of ethanol is 60 mg/dm^3
b) curve 5 - dose of ethanol is 60 mg/dm^3; curves 6, 8, 10 - dose of ethanol is 125 mg/dm^3
The numbers near the curves correspond to the sequence of the experiments (day of the experiment)

Similarly, sulfate reduction is affected by the concentration of sulfate ions. The denitrification of model water that does not contain sulfates (nitrate-containing water with the addition of ethanol was prepared on a distillate) is accompanied by the suppression of sulfate-reducing bacteria, and hydrogen sulfide is not detected in biofiltrate samples. It is important to note that ethyl alcohol, which is dosed into denitrified water, is almost completely consumed in the biofilter. It is always assimilated by the microbiome during the time the treated water is inside the biofilter. This is confirmed by the results of chromatographic studies of water samples supplied to biofiltration denitrification and biofiltrate samples that have been taken from functioning filter at its outlet and from zones of connection of inlet and outlet elbows.

Conclusions

Recently, biological denitrification is increasingly considered as one of available alternatives to decentralized water treatment. Therefore, it is relevant to study the impact of other impurities contained in natural waters, in particular sulfates, carbonates, etc., both on the removal of nitrates directly from the treated water and on its quality. The paper presents the results of denitrification of water in the presence of sulfates in a small-sized submersible biofilter. It is shown that the processes of biotransformation of nitrates and sulfates follow the trajectory of water movement in the biofilter sequentially. Reduction of sulfates to hydrogen sulfide begins after removal of nitrates from the treated water. This happens when the dosage of nutrient substrate (ethanol) added to the biofilter exceeds the stoichiometric amount required for denitrification. The obtained results in subsequent studies can be used to further improve the quality of the obtained biofiltrate due to the additional removal of impurities of salts of heavy and polyvalent metals from it.

Acknowledgements

None.

Conflict of Interest

None.

References

Abascal, E., Gómez-Coma, L., Ortiz, I., & Ortiz, A. (2022). Global diagnosis of nitrate pollution in groundwater and review of removal technologies. *Sci. Total Environ*., 810, article number 152233. doi: 10.1016/j.scitotenv.2021.152233.

DOI: 10.24025/2306-4412.3.2023.278907

Alguacil-Duarte, F., González-Gómez, F., & Romero-Gámez, M. (2022). Biological nitrate removal from a drinking water supply with an aerobic granular sludge technology: An environmental and economic assessment. *J. Clean. Prod*., 367, article number 133059. doi: 10.1016/j.jclepro.2022.133059.

Aslan, S., & Cakici, H. (2007). Biological denitrification of drinking water in a slow sand filter. *J. Hazard. Mater*., 148(1), 253-258. doi: 10.1016/j.jhazmat.2007.02.012.

Benes, V., Pěkný, V., Skorepa, J., & Vrba, J. (1989). Impact of diffuse nitrate pollution sources on groundwater quality-some examples from Czechoslovakia. *Environment. Health Perspect.*, 83, 5-24. doi: 10.1289/ehp.89835.

Besser, H., Dhaouadi, L., & Hamed, Y. (2022). Groundwater quality evolution in the agro-based areas of southern Tunisia: Environmental risks of emerging farming practices. *EuroMediterr. J. Environ. Integr.*, 7(1), 65-78. doi: 10.1007/s41207-021-00289-w.

DSanPiN 2.2.4-171-10. (2023). Retrieved from https://zakon.rada.gov.ua/laws/show/z0452-10#Text:vilnyi. Accessed: Jan. 1.

Duran Romero, D.A., De Almeida Silva, M.C., Chaúque, B.J.M., & Benetti, A.D. (2020). Biosand filter as a point-of-use water treatment technology: Influence of turbidity on microorganism removal efficiency. *Water*, 12(8), article number 2302. doi: 10.3390/w12082302.

Fewtrell, L. (2004). Drinking-water nitrate, methemoglobinemia, and global burden of disease: A discussion. *Environment. Health Perspect.*, 112(14), 1371-1374. doi: 10.1289/ehp.7216.

Freitas, B., Terin, U., Fava, N. et al. (2022). A critical overview of household slow sand filters for water treatment. *Water Res*., 208, article number 117870. doi: 10.1016/j.watres.2021.117870.

Gevod, V.S., Chernova, A.S., & Issayeva, A.U. (2021). Comparison of direct flow and displacement biofiltration in decentralized water treatment devices. *Visnyk Cherkaskogo derzhavnogo tekhnolohichnogo universytetu*, 1, 162-172. doi: 10.24025/2306-4412.1.2021.229015.

Grout, L., Chambers, T., Hales, S. et al. (2023). The potential human health hazard of nitrates in drinking water: A media discourse analysis in a high-income country. *Environ. Health*, 22(1), article number 9. doi: 10.1186/s12940-023-00960-5.

He, Q., He, Z., Joyner, D.C. et. al. (2010). Impact of elevated nitrate on sulfate-reducing bacteria: A comparative study of Desulfovibrio vulgaris. *ISME Journal*, 4(11), 1386-1397. doi: 10.1038/ismej.2010.59.

Herasymchuk, L., Romanchuk, L., & Valerko, R. (2022). Water quality from the sources of non-centralized water supply within the rural settlements of Zhytomyr region. *Ekologia Bratislava*, 41(2), 126-134. doi: 10.2478/eko-2022-0013.

Jensen, V.B., Darby, J.L., Seidel, C., & Gorman, C. (2012). Drinking water treatment for nitrate. Technical report 6. *Addressing Nitrate in California's Drinking Water with a Focus on Tulare Lake Basin and Salinas Valley Groundwater.* Report for the State Water Resources Control Board Report to the Legislature. Center for Watershed Sciences, University of California, Davis, 2012. Retrieved from https://groundwaternitrate.ucanr.edu/index.cfm.

Maiyo, J.K., Dasika, S., & Jafvert, C.T. (2023). Slow sand filters for the 21st century: A review. *Int. J. Environ. Res. Public Health*, 20(2), article number 1019. doi: 10.3390/ijerph20021019.

Matei, A., & Racoviteanu, G. (2021). Review of the technologies for nitrates removal from water intended for human consumption. In *IOP Conference Series: Earth and Environmental Science*, 664(1), article number 012024. doi: 10.1088/1755-1315/664/1/012024.

DOI: 10.24025/2306-4412.3.2023.278907

Mohobane, L., Mutsvangwa, C., & Asante, Y.O. (2022). Removal of nitrate in raw water using a vertical roughing filter with an external carbon source. *Water Environ. J.*, 37(1), 4-25. doi: 10.1111/wej.12813.
Mohseni-Bandpi, A., Elliott, D.J., & Zazouli, M.A. (2013). Biological nitrate removal processes from drinking water supply - a review. *J. Environ. Health Sci. Eng.*, 11(1). doi: 10.1186/2052-336x-11-35.
Mutsvangwa, C., & Matope, E. (2017). Use of an external organic carbon source in the removal of nitrates in bio-sand filters (BSFs). *Drink. Water Eng. Sci.*, 10(2), 119-127. doi: 10.5194/dwes-10-119-2017.
National report on the quality of drinking water and the state of drinking water supply in Ukraine in 2021. (2022). Retrieved from https://www.minregion.gov.ua/wp-content/uploads/2022/12/naczionalna-dopovid-pro-yakist-pytnoyi-vody-ta-stan-pytnogo-vodopostachannya-v-ukrayini-u-2021-roczi.pdf vilnyi.
Noori, R., Farahani, F., Jun, C. et al. (2022). A non-threshold model to estimate carcinogenic risk of nitrate-nitrite in drinking water. *J. Clean. Prod*., 363, article number 132432. doi: 10.1016/j.jclepro.2022.132432.
Paradis, D., Vigneault, H., Lefebvre, R. et. al. (2016). Groundwater nitrate concentration evolution under climate change and agricultural adaptation scenarios: Prince Edward Island, Canada. *Earth Syst. Dyn*., 7(1), 183-202. doi: 10.5194/esd-7-183-2016.
Piskarev, I.M., Ushkanov, V.A., Aristova, N.A. et al. (2010). Establishment of the redox potential of water saturated with hydrogen. *Biophysics*, 55(1), 13-17. doi: 10.1134/s0006350910010033.
Rocher, V., Mailler, R., Mèche, P. et al. (2019). Clogging limitation of nitrifying biofilters: BiostyrDuo® process study. *Water Pract. Technol*., 14(1), 43-54. doi: 10.2166/wpt.2018.107.
Romanchuk, L.D., Valerko, R.A., Herasymchuk, L.O., & Kravchuk, M.M. (2021). Assessment of the impact of organic agriculture on nitrate content in drinking water in rural settlements of Ukraine. *Ukr. J. Ecol*., 11(2), 17-26. doi: 10.15421/2021_71.
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. doi: 10.22093/WWJ.2020.201484.2928.
Sidiropoulos, P., Tziatzios, G., Vasiliades, L. et al. (2019). Groundwater nitrate contamination integrated modeling for climate and water resources scenarios: The case of Lake Karla over-exploited aquifer. *Water*, 11(6), article number 1201. doi: 10.3390/w11061201.
Temkin, A., Evans, S., Manidis, T., Campbell, C., & Naidenko, O.V. (2019). Exposure-based assessment and economic valuation of adverse birth outcomes and cancer risk due to nitrate in United States drinking water. *Environ. Res*., 176, article number 108442. doi: 10.1016/j.envres.2019.04.009.
Ward, M., Jones, R., Brender, J. et al. (2018). Drinking water nitrate and human health: An updated review. *Int. J. Environ. Res. Public Health*, 15(7), article number 1557. doi: 10.3390/ijerph15071557.

DOI: 10.24025/2306-4412.3.2023.278907

МАТЕМАТИЧНА МОДЕЛЬ СПОЛУЧЕНИХ ПРОЦЕСІВ ДЕНІТРИФІКАЦІЇ ТА ВІДНОВЛЕННЯ СУЛЬФАТІВ В ІННОВАЦІЙНОМУ БІОФІЛЬТРІ

І. О. Борисов
Аспірант
Державний вищий навчальний заклад
«Український державний хіміко-технологічний університет»
49005, просп. Гагаріна, 8, м. Дніпро, Україна
https://orcid.org/0000-0003-0982-245X
В. С. Гевод
Доктор хімічних наук, ст. дослідник
Державний вищий навчальний заклад
«Український державний хіміко-технологічний університет»
49005, просп. Гагаріна, 8, м. Дніпро, Україна
https://orcid.org/0000-0002-5027-6916
e-mail: aquilegya@ua.fm

Анотація. В роботі із застосуванням математичного моделювання розкрито особливості біологічного перетворення нітратів і сульфатів до нітрогену та сірководню під дією гетеротрофних денітрифікаційних і сульфат-відновлювальних бактерій в малогабаритному заглибному біофільтрі при різних співвідношеннях «карбон/нітроген». Технологія біофільтрації дає змогу виробляти питну воду більш екологічно безпечним, економічним та ефективним способом. Однак підземні води, окрім небезпечних для здоров'я людини нітратів, містять й інші неорганічні сполуки (солі важких та полівалентних металів, карбонати, сульфати і т. д.), що беруть участь у супутніх процесах (метаногенезу, сульфат-відновлення, уреолізу) в біофільтрі. Під час дослідження було розкрито додаткові можливості денітрифікаційного малогабаритного заглибного біофільтра, а саме, біотрансформації разом із нітратами сульфатів до сірководню, який може сприяти видаленню іонів важких та полівалентних металів з води. Досліджено зрушення сульфат-сульфідної рівноваги у водному середовищі біофільтра та вплив концентрацій сульфат-іонів і субстрату бактеріального живлення, зокрема етанолу, на накопичення і його витрачання в об'ємі біофільтра при здійсненні біофільтраційної денітрифікації. Результати моделювання сполучених процесів денітрифікації води у малогабаритному інноваційному біофільтрі у присутності сульфатів дали змогу встановити можливість і чинники їх керованого відновлення. Показано, що перевищення дозування субстрату живлення (етанолу) у вихідну воду порівняно зі стехіометричним, коли «карбон/нітроген» дорівнює 0,94, призводить до появи у фільтраті сірководню, який продукують сульфат-відновлювальні бактерії за рахунок живлення залишками етанолу. Сірководень у фільтраті не з'являється при дозуванні субстрату живлення у вихідну воду в кількості, що відповідає показнику «карбон/нітроген» меншому, ніж потребує стехіометрія біологічного відновлення нітратів. Кероване відновлення сульфатів до сірководню може бути корисним додатковим інструментом поліпшення якості фільтрату при сумісній денітрифікації і вилученні з води домішок солей важких металів. Розроблена модель і отримані результати можуть бути використані для подальшого поліпшення якості одержуваного біофільтрату за рахунок додаткового видалення з нього домішок солей важких і полівалентних металів.

Ключові слова: децентралізоване водоочищення, нітрати, сірководень, бактеріальне живлення, якість води.

Дата надходження: 10.05.2023
Прийнято: 07.09.2023

DOI: 10.24025/2306-4412.3.2023.278907