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WATER DENITRIFICATION BY DISPLACEMENT BIOFILTRATION: TRANSITION OF DESIGNED BIOFILTER TO THE STATIONARY MODE

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This work was aimed at creating a simple and reliable submersed biofilter for the decentralized treatment of nitrate-contaminated water. Denitrification of water was performed by the method of displacement (piston) biofiltration in specially designed U-shaped devices intended for residential use. The efficiency of biofiltration in these devices was evaluated under the conditions of their continuous service. The biofilter exhibited an essential increase in the rate of denitrification when transferring to the stationary mode. Hence, the consumer will have the opportunity of supplying big portions of nitrate-contaminated water into the biofilter in one gulp (pulse) and simultaneously getting the same amount of deeply denitrified water. This mode of biofilters exploitation prevents the clogging of the filtration bed and the channeling in it. The design of the created biofilters is rather simple. Materials with a minimum carbon footprint can be used to fabricate these devices.

Keywords: biofilter, denitrification, displacement biofiltration, drinking water, stationary mode.

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Introduction

The problem of deterioration of quality of the groundwater sources is a topical issue becomes in the last decades. At present, the water from wells and boreholes very often exhibits the concentration of nitrate that violates sanitary and hygienic regulations. An excessive concentration of nitrates in drinking water causes methemoglobinemia in infants and provokes malignant tumors and other dangerous diseases in adults [1]. Known means [2] of nitrates removal from the groundwater are not appropriate to solve the problem because they are too expensive at installation and operation.

U-shaped biofilters seem to be a good alternative to ensure cost-effective denitrification of nitrates polluted water at the point of use. This work was aimed at evaluating the efficiency of nitrate removal by these devices during their continuous service [3,4]. The main attention was devoted to the regimes of biofiltration. The rate of biofiltration was determined as a function of periodicity and irregularity of water supply for the treatment.

Results and discussion

Experimental technique was described in detail elsewhere [5].

The results of the study of displacement biofiltration for nitrates removal during long-term service are given in Fig. 1. The left-hand side in this figure shows the influence of nitrate concentration in the entering water on nitrates concentration in the filtrate. One can see a very weak (soft) interconnection between nitrate concentration in the water supplied and nitrate concentration in the treated water. Nitrate concentration in the filtrate does not exceed few milligrams per liter even when the entering portions of water contain about 700–800 mg L^{-1} of nitrate.

A sharp increase in the concentration of nitrates in portions of water supplied to processing does not lead to exceeding the legalized sanitary-hygienic level of nitrates in the filtrate. These results relate to the final part of a long-continued test (one year's) of a manufactured biofilter in a displacement biofiltration mode. After that, there was a two-month shutdown. During the break, the biofilter remained filled with water, and natural microbiological reactions occurred inside it without interference from the outside. At the end of the break time, the concentration of nitrates was measured in the inlet and outlet of the biofilter as well as at its bottom. The nitrate

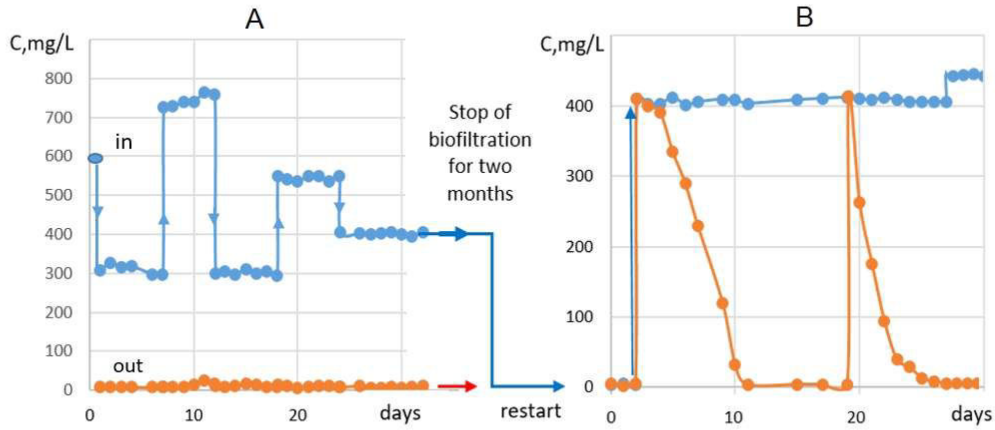

Fig. 1. A – Influence of nitrate concentration in the portions of supplied water on nitrate concentration in the portions of received filtrate for displacement biofiltration. B – A restart of displacement biofiltration after two-month shutdown. Explanations are given in the main text

concentration was at a minimum detectable level ensured by the ion-selective electrode. The concurrent visual inspection of the device revealed the disappearance of biofouling on the inner surfaces of the biofiltration case below the fluid level. Bacteria that formed biological fouling in the period of their active functioning (i.e. when was enough quantity of easily assimilated carbon and nitrates in the processing water) used the biofouling matter to preserve their vitality when gone into unfavorable living conditions. At the same time, black dots were observed here and there. This is a characteristic sign of bacterial activity dealt with the biological reduction of sulfates. Water samples taken from the bottom of the apparatus showed the presence of hydrogen sulfide.

Figure 1, B shows to what extent the biofilter retains the ability to denitrify water after a two-month break. The initial point in this graph corresponds to the state when the water with the initial concentration of sodium nitrate 400 mg L^{-1} (4.7 mM $NaNO_3$+5 mM C_2H_5OH) was added to the biofilter after thorough washing of filtration bed by water with a certain concentration of nitrates. When the apparatus has come back to run in the mode of displacement biofiltration, a rapid decrease in the nitrate concentration was observed at the exit of the biofilter following a lag phase of approximately two days. This indicates that a two-month break in the biofilter use did not lead to the decay or death of denitrifying microflora. With the resumption of favorable conditions, the denitrifying microflora began to function properly again. To ensure that this is true, the subsequent portions of water (2.5 liters in one gulp) with the depicted nitrate and alcohol concentration were fed irregularly to the biofilter inlet on different days. The points in the upper curve of Fig. 1,B for time interval 10–20 days show the exact data concerning the addition of the portions of water to biofiltration. No noticeable deviations in the concentration of nitrates in the filtrate were detected as compared with the values measured before the shutdown of the device. After that, the filter was rewashed by water with a nitrate concentration of 400 mg L^{-1} with the addition of the required quantity of ethyl alcohol, and biofiltration continued to run in displacement mode with regular supplying the portions of nitrate-contaminated water. In this case, the kinetics of nitrate concentration reduction did not differ from that observed at first switching on the apparatus. The concentration of nitrates measured at the entry and bottom points of the receiving elbow every day after supplying the previous portion of nitrate-contaminated water to the biofilter was close to a few milligrams per liter. This phenomenon is illustrated by the position of the heads of arrows in Fig. 2,A,B. Only one day is required for decreasing the nitrate concentration in the water inside the entering elbow of the biofilter by many times. The result shows that the colonies of denitrification bacteria grow in a steady-state mode and exhibit maximum activity at the part of the filtration bed where the environmental conditions are the most favorable. That is the inlet zone of the biofilter where the concentrations of nitrates and easily assimilated carbon (ethanol) are sufficient for rapid constructive and energy exchanges in bacterium cells. These results are consistent with those published elsewhere [6,7]. Gomez et al. [6] studied the influence of ethanol concentration on biofilm functioning in denitrifying submerged biofilter used for processing contaminated groundwater. Under the steady-state conditions of

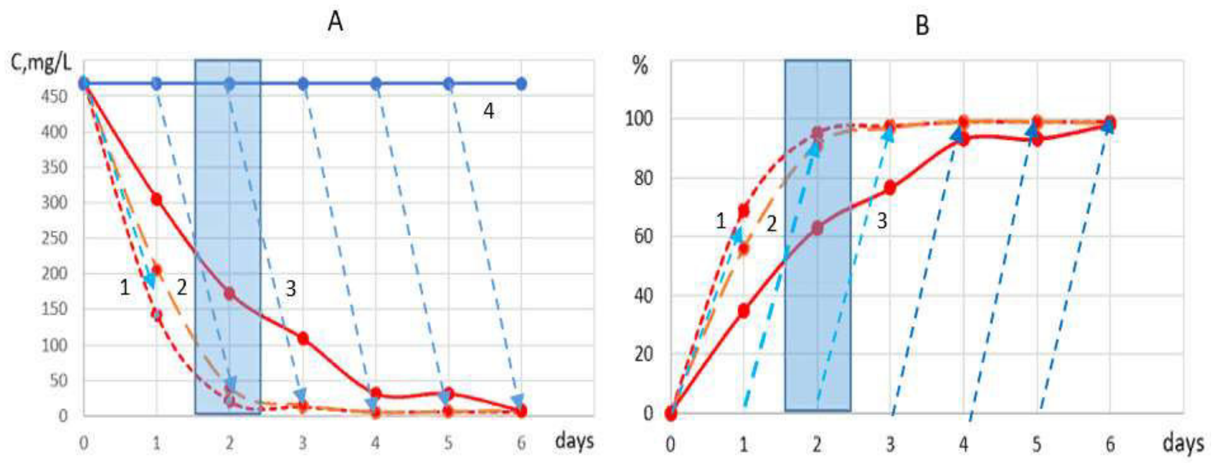

Fig. 2. Kinetics of nitrate concentration reduction (A) and percentage of nitrate removal (B) in the biofilter at the displacement biofiltration: 1 – in the entering zone of the biofilter at its transition to the stationary mode; 2 – in the bottom part of biofilter at its transition to the stationary mode; 3 – at the exit of the biofilter at its start to run after washing. The arrows depict the concentration of nitrates measured the next day after adding the previous portion of water to processing; 4 – the concentration of nitrates in the portions of supplied water

biofilter operation, the prevailing reduction of nitrate concentration and a decrease in ethanol content were observed at the entering distance of the filtration pathway. The number of counted denitrifying bacteria was also increased. The result showed that a higher ethanol and nitrate concentrations promote better energy yield inside the entering zone of the biofilter and, therefore, greater proliferation of bacteria that consume carbon and nitrates.

Zuniga [7] performed a theoretical study concerning nitrate concentration and the biomass profiles in the model of the submerged biofilter under the static and dynamic conditions. A distributed parameter system was considered in which the biofilter state variables were analyzed in both time and space by partial differential equations that describe the mass balance of each component. The modeling showed a directly proportional decrease of nitrate and ethyl alcohol concentrations with time at the entering zone of the biofilter. As for denitrification biomass distribution along the biofiltration body is concerned, the modeling also showed the accumulation of denitrifying biofilms at the short entrance part of the biofiltration pathway with the maximum density not far from the point of water entering the filtration bed.

In such a way, the denitrification of the water occurs in the created biofilter with different rates depending on the state of denitrification biofouling on the grains of the filtration bed. After hydraulic shock accompanied by rough washing and removing water from the biofilter body and the following filling it with the water to be treated, the rate of denitrification is moderately low. In the stationary phase, the rate of denitrification increases by many times. In this state, the reaction obeys the zero-order kinetics. An important feature of the microflora action in the biofilter is the auto-induced consumption of excessive biomass. The particulates of biofouling, which detached from the mother's body at the initial (incoming) part of the filtration pathway (at the adding portions of water by one gulp into the entering elbow of the biofilter), are partially consumed by the «hungry» bacterium inside of the exit elbow. To process planktonic matter and convert it into nitrogen gas, the bacteria use dissolved oxygen and oxygen from the rest nitrates. The chemical equations that described this process are as follows [8]:

$$5O_2+C_5H_7O_2N \rightarrow 5CO_2+NH_3+2H_2O; \quad (1)$$

$$NO_3^- + 0.25C_5H_7O_2N \rightarrow$$
$$\rightarrow 1.25CO_2 + 0.25NH_3 + OH^- + 0.5N_2. \quad (2)$$

When the nitrate concentration becomes close to zero, the sulfate reduction bacteria start to dominate in the biofiltration system in the presence of alcohol. The main equation of this process is as follows [9]:

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

The hydrosulfide ion undergoes hydrolysis releasing the hydrogen sulfate:

$$HS^- + H_2O \rightarrow H_2S + OH^-. \quad (4)$$

When hydrogen sulfide interacts with the cations of heavy and polyvalent metals, insoluble sulfides and hydroxides of these metals are formed. Microbiological reduction of sulfates into hydrosulfides and hydrogen sulfide occurs much slower than denitrification. The removal of hydrogen sulfide, insoluble sulfides and hydroxides is described in refs. [10,11].

The designed biofilter is a self-regulating system. Its nitrates removal capacity increases manifold during its continuous run as shown in Fig. 3. The columns with indexes y1 show the kinetics of the sequential supplying discrete portions of nitrate-contaminated water to biofiltration. The initial concentration of nitrates in these portions was 200 mg L^{-1}. The volume of portions was 2.5 L and 1.7 L at the heterotrophic and autotrophic denitrification, respectively. The heights of the columns with indices y2 and y3 show the nitrate concentrations in the sequentially shifting portions of water when autotrophs and heterotrophs provide the removal of nitrates, after rough washing the biofiltration bed. The heights of the columns with indices y4 show the nitrate concentrations in the water of entering elbow measured at steady-state functioning of this device in the displacement mode (daily feeding by chosen portions of nitrate-contaminated water with the required quantity of ethyl alcohol and measuring nitrate concentration inside the top and bottom zones in the entering elbow the next day).

Regular (in one gulp) supply of portions of water to the denitrifying biofilter ensures normalization of the activity of denitrifying biofouling in the pore space. This increases the stability of the biofilter run and eliminates the need for special dosing and flushing devices. At this mode of action, the biofilter becomes able to work for a long time without clogging and channeling.

Conclusions

Decentralized removal of nitrates from the water of problematic sources can be carried out by an environmentally friendly method in the device of point of use, a submersed biofilter of the proposed design. The essence of the method consists in the implementation of the displacement biofiltration. It is a process where water is supplied by separate portions (pulses) to the inlet of the biofilter. These portions are sequentially shifted through the granular load with incubated colonies of denitrifying bacteria. At the exit of the biofilter, the consumer simultaneously gets the same portions of denitrified water. In the designed apparatus, the denitrification rate increases many folds in the course of its exploitation. It occurs as a result of shifting the main denitrification zone to the entrance of biofilter, where the best ecological niche for denitrifying bacteria arises. The shape of the biofilter and the overall length of the filtration pathway allow getting sustainable

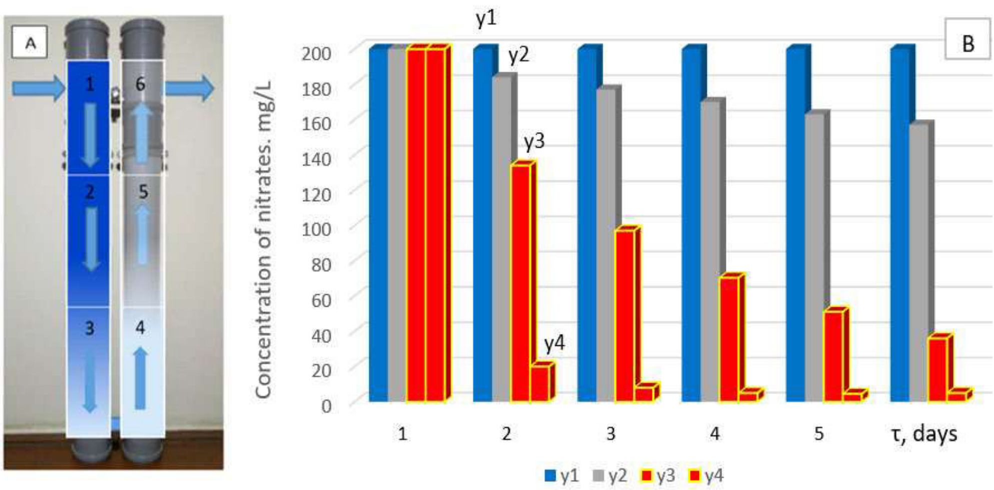

Fig. 3. A – Sequence of shifting the portions of water along the biofiltration path in U-shaped devices with HDPE and sulfur and marble filtration beds. B – the results of the measurement of nitrate concentration at the exit (y2, y3) at the start (or restarting) of biofilter operation. Measurements were done with a one-day delay after supplying each previous portion of water to biofiltration. y4 – the concentration of nitrates at the entrance and bottom zones of the biofilter measured with a one-day delay after supplying each previous portion of water to biofiltration at a stationary functioning of the device

denitrification independent of the initial nitrate concentration in water. The designed biofilter can also purify water from heavy metal ions. The shutdown of the biofilter for two months does not impair its ability to purify the nitrate-contaminated water when the operation turns on again. It is due to the auto-induced consumption of excessive biomass by denitrifying bacteria for survival when the biofilter switches off for a long time. A comparison of the functioning efficiency of autotrophic and heterotrophic bacteria in the studied filtration beds suggests that each of them can be used to denitrify water. Heterotrophic denitrification is preferable in small-scale devices since the heterotrophic denitrifying bacteria process nitrates much faster than the autotrophic bacteria. As a result, the following benefits appear:

– there is no need to use special means to ensure required slow flows of denitrified water through the bio-filter;

– the consumer gets the ability to direct big portions of water in one gulp for biofiltration and at the same time receive equal portions of denitrified water;

– manufacturing of biofilters with the developed design and their operation do not require unjustified material and energy consumptions. These devices can be made of materials with a minimal carbon footprint.

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ДЕНІТРИФІКАЦІЯ ВОДИ МЕТОДОМ ВИТИСНЮВАЛЬНОЇ БІОФІЛЬТРАЦІЇ: ПЕРЕХІД СТВОРЕНОГО БІОФІЛЬТРА ДО СТАЦІОНАРНОЇ РОБОТИ

В.С. Гевод, А.С. Чернова

Ця робота мала на меті створити простий і надійний занурений біофільтр для децентралізованої обробки води, що забруднена нітратами. Денітрифікація води була здійснена методом витиснювальної (поршневої) біофільтрації в спеціально розроблених U-подібних пристроях, призначених для домашнього застосування. Було здійснено оцінювання ефективності біофільтрації за умов тривалої експлуатації. Біофільтр продемонстрував істотне збільшення швидкості денітрифікації при переході до стаціонарного режиму роботи. У результаті споживач отримує можливість подавати великі порції забрудненої нітратами води в біофільтр залпом (імпульсом) і одержувати синхронно рівну кількість глибоко денітрифікованої води. Цей режим роботи біофільтрів запобігає засміченню фільтруючого шару та утворенню каналів в ньому. Дизайн створених біофільтрів простий. При виготовленні цих пристроїв можна використовувати матеріали з мінімальним вуглецевим відбитком.

Ключові слова: біофільтр, денітрифікація, режим витіснення, питна вода, стаціонарний режим.

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