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Sulfur Utilization in the Systems of Biological Wastwater Denitrification

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Abstract. This paper focuses on the study of the possibility of using mineral carriers from sulfur (bio-sulfur/elementary sulfur) in anaerobic wastewater treatment systems under autotrophic denitrification conditions. The theoretical aspects of the work are based on the biochemical formalization of the studied processes using the system-ic-synergetic approach for the description of the patterns of autotrophic denitrification microorganisms based on the principles of autocatalysis of natural systems. Special software was used in the work to identify the necessary ecological and trophic groups of microorganisms and implement the schemes of trophic interactions in association of denitrification microorganisms. The taxonomic classification was assigned based on the KEGG database (Kyoto Encyclopedia of Genes and Genomes). Bio-filtration set-up system was formed for carrying out the process wastewater denitrification with using bio-sulfur and gaseous sulfur. The filtration method is used under anaerobic conditions along with immobilization on the carrier based on sulfur autotrophic denitrifying bacterial species such as Thiobacillus denitrificans and Thiomicrospira denitrificans. Thus, sulfur conversion leads to the reduction of nitrates to nitrites and, ultimately, the release of molecular nitrogen. The mechanisms of sulfur conversion in natural ecosystems make it possible to conclude its expediency of use it as a sorption sulfur-containing mineral carrier in wastewater purification systems with further conversion to an organic form (with microbial cell carbonate). The interactions pathways model in the association of heterotrophic and autotrophic denitrification bacteria in the process of wastewater and sewage sludge purification was formed under condition of elementary sulfur presence. Energetic and synthesis reactions for an autotrophic denitrification were described. The implementation of wastewater treatment systems with autotrophic denitrification process use will provide an opportunity to expand the application scope of by-products such as gaseous sulfur and bio-sulfur that currently minimal recycling in traditional industrial processing.

Keywords: denitrification, bio-sulfur, gaseous sulfur, wastewater, mineral carrier.

1 Introduction

Sulfur is one of the main types of chemical raw for materials, which have strategic importance for the country's economy. Due to continuing growth of population and areas under cultivation, it is required an intensification of agriculture, which significantly depends on the introduction of mineral and organic fertilizers that contain sulfur [1].

Ecological aspects of sulfur application during obtaining sulfuric acid is the emission of such harmful substances as acid fog and sulfurous anhydride SO_2. Moreover, in gas sulfur, which is a waste of the process of purification of gases of petroleum processing, non-ferrous metals, associated petroleum and natural gases can contain arsenic and other harmful impurities [2], which, with the open method of storing of gas sulfur can migrate to the environment.

The emergence of the problem of elemental sulfur as a large-capacity technogenic formation is connected with the existence of a stable disproportion between the process of its accumulation in the environment and the consumption reduction in traditional areas (sulfuric acid production, paper-and-pulp industry, etc.). There is an urgent need to diversificate the application of sulfur, particularly the materials production based on its ground in order to apply them in filtration biotechnological waste water treatment systems [3].

Another important mission of the environmental safety is the deprivation of nutrients from wastewater, which after getting into surface water cause significant damage to the ecological system for the region, and this requires an effective discharge treatment from such compounds (nitrogen and phosphorus, in particular).

Nitrates are considered to be the most widespread type of inorganic pollutants that contribute to rapid development of blue-green algae and other lower plants with short life cycles for the decomposition course of decaying organic matter of which a large amount of the oxygen dissolved in water is consumed leading to decaying of the dominant groups of aquatic organisms. At the same time, nitrates cause great harm to the human body, generally due to their consecutive transformation into nitrites and nitro compounds which belong to carcinogenic substances. In ground waters, nitrates are accumulated due to transfer sewage disposal chemical and petrochemical factories in them, as well as the fertilizers which are washed away from agricultural fields, drains of cattle farms. Nitrate content may vary depending on chemical and biological composition of soils [4].

Thus, the possibility of a unified approach developing to solve the problem of removing nitrogen compounds from liquid waste and using nonorganic sulfur varieties in biological denitrification systems is of great importance in reducing the environmental footprint in the region. In our opinion, the expansion of biosulfur using as a product of gas flows biodesulfurizationis, which is possible due to its application together with gas sulfur in biofiltration systems for removing nitrates from effluents, which requires further scientific, theoretical and experimental evidence.

2 Literature Review

Among the methods for effluents purification from nitrates, a special niche is occupied by biological methods of denitrification, which are divided into autotrophic and heterotrophic.

Anaerobic activated sludge is used in many studies for restoration of nitrites and nitrates in the process of denitrifying sewage. Denitrifying bacteria are found among representatives of Acrobacterium sp. and others, which, being in anoxic conditions, use oxygen for breathing that contained in nitrites and nitrates instead of dissolved oxygen. Herewith, most of the studies focused on studying and increasing the effectiveness of the use of heterotrophic bacterium-denitrifying agents which represent a group of facultative anaerobes. This is facilitated by the fact that they are present in the sewage in large quantities and can use pollutants as a carbon feed (methanol, ethanol, acetic acid), greatly facilitates the exploitation of structures, as it eliminates the need to grow a special adapted microflora [5].

Downflow denitrification filters operate in a conventional filtration mode and consist of media and support gravel supported by an underdrain. Wastewater enters a downflow filter over weirs along the length of the filter bed on both sides.

Filter effluent is conveyed from the bottom of the filter over a control weir into a clear well. During the process, nitrate is metabolized to nitrogen gas, which becomes embedded in the filter media. Nitrogen-release cycles are needed to remover these nitrogen gas bubbles that accumulate. The piping for the filter influent and backwash is similar to that of conventional filters.

Wastewater enters the filter through the influent pipe and then is transported downward through a supply pipe and distributors (Figure 1). The water moves up through the filter media and filtrate is discharged from the upper portion of the filter.

The preferred media for each filter manufacturer is also presented in Table 1.

Separate-stage denitrification can be carried out either as a suspended or attached growth process, both of which require an external carbon source, such as methanol. Because they require a large area and their own sludge settling and recycling system, separate suspended growth denitrification systems are not very common (Figure 2).

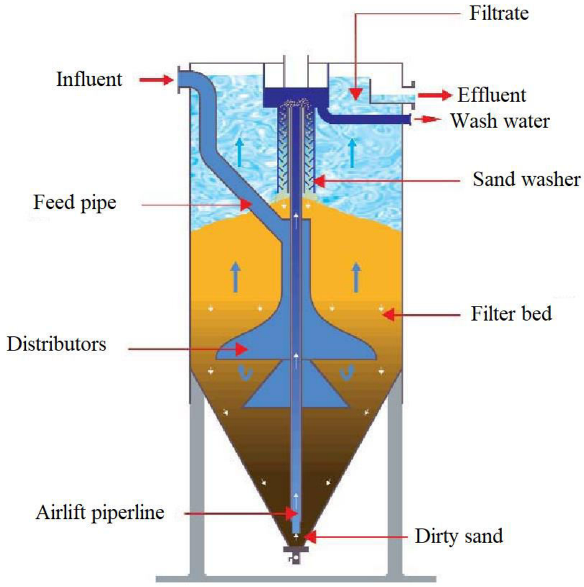

Figure 1 – Astrasand upflow continuous - backwash filter

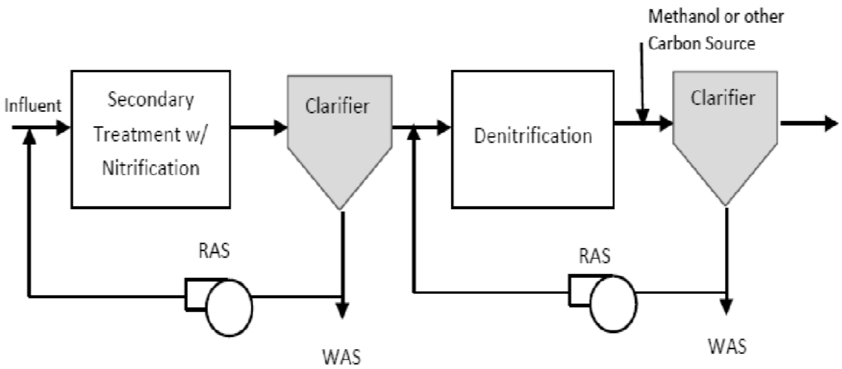

Figure 2 – Separate-stage suspended growth denitrification process

Table 1 – Filtration material in denitrification systems [6]

Manufacturer / filter	Severn Trent Services/ TETRA® Denite®	F. B. Leopold / elimi-Nite	USFilter/Davco	Parkson / DynaSand	Paques and USFilter/ Astrasand
Flow regime	Downflow	Downflow	Downflow	Upflow	Upflow
Media	457 mm (18 in) graded gravel, 1.8 m (6 ft) of 6×9 mesh silica sand, uniformity coefficient 1.35, 0.8 minimum sphericity	381 mm (15 in) graded gravel, 1.8 m (6 ft) of 6×12 mesh sand	2 layers support gravel, 1.8 m (6 ft) of 6×9 mesh sand	1.35 to 1.45 mm subround media or 1.55 to 1.65 mm subangular media with uniformity coefficient of 1.3 to 1.6; 2-m (6.6 ft) bed depth	1.2 to 1.4 mm sand, 2-m (6.6-ft) bed depth

Denitrification filters are popular, because they are an easy retrofit and require less area and sludge handling. The units can simply be added to the end of a secondary treatment process that includes nitrification. Both downflow and upflow filters are in use. Downflow filters require backwashing to remove solids and nitrogen gas trapped in the filter media. Upflow filters skirt this problem by having the filter media continuously removed from the bottom of the unit, cleaned, and recycled to the top of the filter (Figure 3) [7].

The main components of a modern Continuous Activated Sludge Biological Nutrient Removal (BNR) systems are presented in Figure 4.

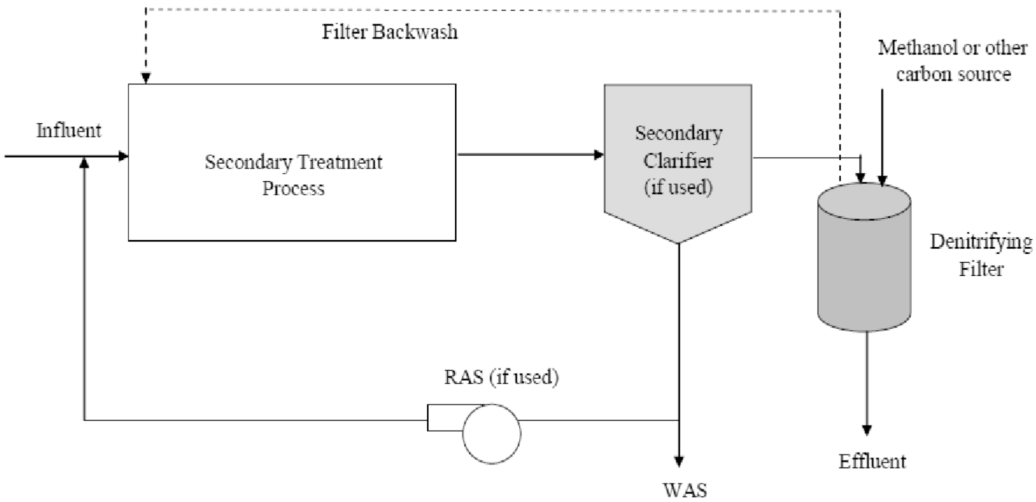

Figure 3 – Separate-stage denitrification filter process

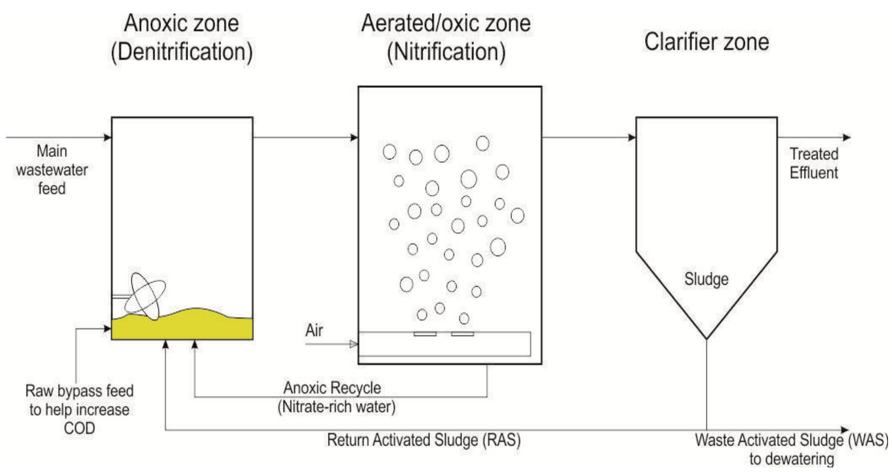

Figure 4 – Continuous Activated Sludge BNR systems

The anoxic (denitrification) basin or zone continually receives several streams including the main feed of ammonia-rich wastewater from the upstream anaerobic pond. This is a large volume stream containing the bulk of the new nitrogen load to the system. Unfortunately, the COD content of this stream is usually insufficient to provide all the COD needed for the denitrifying bacteria so additional COD is added [8].

In autotrophic denitrification, sulfur or hydrogen is used by microorganisms as a source of energy.

The continuously stirred tank reactor (CSTR) that capable of providing an adequate seed source of autotrophic denitrifiers was used in the study [9]. As shown in Figure 5, anaerobic upflow fixed-bed reactor was constructed from 2.5-inch I.D. acrylic tubing with four sampling ports. The empty bed reactor volume is 1.11 liters. The sulfur and limestone grain sizes ranged from 2.38 mm to 4.76 mm. Gas collection and monitoring systems have been included in this design.

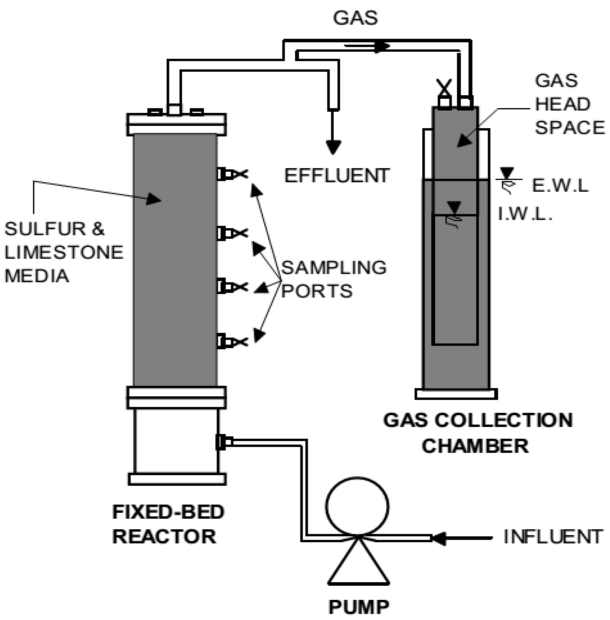

Figure 5 – Upflow fixed-bed column reactor [9]

The feed solution composition for the CSTR: KNO_3, 3.0 g/l; $Na_2S_2O_3{\cdot}5H_2O$, 6.0 g/l; $NaHCO_3$, 1.5 g/l; Na_2HPO_4, 1.5 g/l; KH_2PO_4, 0.3 g/l; $MgSO_4{\cdot}7H_2O$, 0.4 g/l; and 1 ml of stock trace nutrient solution per liter of feed solution [9].

However, these methods need to be improved. These disadvantages are water pollution residual methanol or sulfur, and a large content of microorganisms in the treated water. In addition, this process is characterized by increased sensitivity to temperature conditions, and its rate decreases in cold water, which makes it difficult to use biological denitrification in regions with a cold climate [4].

In [10], methods for the oxidation of ammonium and a hardly available organic matter of wastewater are offered in aerobic-anoxid conditions. To carry out the process of simultaneous autotrophic and heterotrophic denitrification, a batch reactor with a volume of 61 dm^3 was built.

A complete retention of the biomass of the active sludge was carried out in the reactor, the residence time of the liquid was 2,5-5 days, the sludge dose was 1.5–2.5 g/dm^3, the temperature was 20-28 °C, and the pH was 7.5-8.5. The concentrations of ammonium nitrogen and nitrogen nitrite in renovated water were 0.3-8 mg/dm^3 and, accordingly, 0.2-4 mg/dm^3 (Table 2) [10]. The efficiency of nitrogen removal was 91% -80% due to the process of autotrophic denitrification and 11 % due to the heterotrophic denitrification process.

Table 2 – Composition of water received for treatment and after treatment in two successive reactors

Parameter	Crude filtrate	Nitrifiable filtrate	Refined filtrate
$N\text{-}NH_4$, mg/dm^3	250–300	100–120	0.3–8.0
$N\text{-}NO_2$, mg/dm^3	–	130–150	0.2–4.0
$N\text{-}NO_3$, mg/dm^3	–	0.4–3.3	5–10
COD, mg/dm^3	150–190	60–120	60–120

During the experiment it was noted that a significant part of the biomass of the microorganisms in this reactor was secured with the walls of the reactor. The ability of microorganisms for effective adhesion was used to increase the reliability of the reactor by increasing the surface area to which microorganisms could be secured.

A plastic load of polyethylene (AnoxKaldnes K1, 30 % of the volume of the reactor) was placed in the reactor. After a while at the loading has developed the biofilm, in which up to 75 % of the biomass of microorganisms was located. The use of this method led to the stabilization of the quality of water purification in the reactor at the same average (removal of 90–92 % of nitrogen).

However, the biological technologies currently available for nitrate degradation are associated with significant drawbacks including: long start-up times and long recovery times after system upsets; the production of biological solids requiring costly treatment and disposal; low organism densities necessitating large footprints to achieve sufficient treatment capacity.

Thus, an important area of research is the immobilization of active biomass on carriers to reduce their leaching from the bioreactor space and the transfer of the process to a continuous technological regime for treating effluents. As well as the introduction of carrier-feed to stimulate the development of autotrophic groups of microorganisms with the minimization of nutrient removal from the system.

Developing biocomposites for natural, nitrate-degrading organisms that are irreversibly retained within these systems and never leave the biofilter, as they are protected from washout, overgrowth, toxicity, and abrupt changes in operation.

This paper focuses on the study of the possibility of using mineral carriers from sulfur (bio-sulfur / elementary sulfur) in anaerobic wastewater treatment systems under autotrophic denitrification conditions.

To achieve the aim, the following tasks were set:

– analytical studies of the possibility of bio-sulfur and gaseous sulfur use as mineral carriers for bacteria growth under autotrophic denitrification conditions;

– development bio-filtration set-up system for carrying out the process wastewater denitrification with using bio-sulfur and gaseous sulfur.

3 Research Methodology

During biochemical processing and in the course of Claus's reactions, all hydrogen sulfide, which was a part of gas-liquid mixes, is used to produce sulfur: bio-sulfurs (from bio-desulfurization systems) [11] and the gaseous sulfur resp., which have both similar physical and chemical properties and some differences features. It should be noted that bio-sulfur is more demanded in the use in agriculture as a component of fertilizers and fungicides [12].

The analysis of the composition of gaseous sulfur is presented in Table 3 and its general form is shown in Figure 6. Gaseous sulphur has the same chemical formula as solid or liquid Sulphur, S_8.

Table 3 – The technological parameters of gaseous sulfur [13]

Parameter (minimum value), %	Norm for technical gaseous sulfur
Sulfur mass fraction	99.2
Water mass fraction	1.0
Refuse burnout mass fraction	0.4
Organic substances mass fraction	0.5
Acids mass fraction in conversion to spirit of sulfur	0.02

Figure 6 – Photo of the gaseous sulfur granules (3–6 mm)

The main stages of bio-sulfur production are described in the block diagram in Figure 7 with an indication of its component composition according to [11].

Diffractometric research and raster microanalysis of the bio-sulfur structure were held (conducted) and the fact, that 60 % of it consist of orthomolecules S_8^0, was determined. Besides, sulfur organic inclusion (S_{org}) and particles of components of transformed granules ($CaSO_4$, H_2O, $CaCO_3$, $Ca_3(PO_4)_2$, etc.) were found.

It should be noted that the presence of additional biogenic elements in the biosulfur will allow to reduce or eliminate the necessity of supply of additional nutrients to the system. Also, calcium fluoride may be present in the bio-sulfur in the presence of fluorine in the composition of secondary mineral raw materials (phosphogypsum) for the production of an immobilized carrier for the systems of biochemical purification of waste gases from hydrogen sulphide. Calcium fluoride is a chemically relatively passive compound.

The theoretical foundations of the work are based on the biochemical formalization of the purification processes using the systemic-synergetic approach for the description of the patterns of autotrophic denitrification microorganisms based on the principles of autocatalysis of natural systems.

Culture-identify approach. Special software was used in the work to identify the necessary ecological and trophic groups of microorganisms and implement the schemes of trophic interactions in associations of microorganisms-denitrifiers.

The taxonomic classification of each read was assigned based on the KEGG database (Kyoto Encyclopedia of Genes and Genomes).

KEGG is a database resource for understanding high-level functions and utilities of the biological system, such as the cell, the organism and the ecosystem, from genomic and molecular-level information. It is a computer representation of the biological system, consisting of molecular building blocks of genes and proteins (genomic information) and chemical substances (chemical information) that are integrated with the knowledge on molecular wiring diagrams of interaction, reaction and relation networks (systems information). Denitrification (nitrate => nitrogen) module M00529 was used for modelling of association of main ecological and trophic groups of microorganisms involved in individual stages of this process. This program provides the definition of basic biochemical reactions, involved enzymes and microorganisms that contain the relevant genes.

4 Results

4.1 Analytical studies of the possibility of bio-sulfur and gaseous sulfur use as mineral carriers for bacteria growth under autotrophic denitrification conditions

Autotroph denitrification explains the thermodynamic instability of nitrates in critical areas or the lack of lysed organic connections.

Apart from organic carbon, some of the denitrifying bacteria can use inorganic substances, such as hydrogen and sulfur, manganese and ferrum in the capacity of donor of electrons. Few researches showed the application of this process for removing the nitrate out of fouled waters, and the sulfur-limestone reactor was used for the autotroph denitrification of waste waters.

Hence, in [14, 15] the possibility of usage of the industrial waste of desulfurizing of flue gases for considerable decrease of the volume of dregs over the cleaning of waste waters. Therewith the main groups of eco-trophic microorganisms are distinguished, which interact in bioorganic cycles of transformation of biogenous elements (Figure 8).

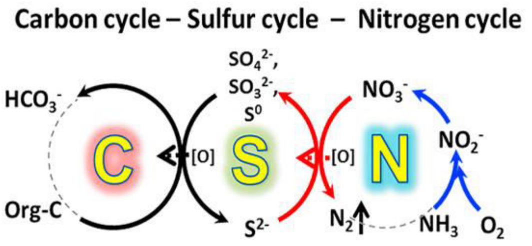

Figure 8 – The scheme of interactions in biochemical cycles between heterotrophic and autotrophic groups of microorganisms used in biological wastewater treatment [15]

The possibility of denitrification in low ratio COD (chemical oxygen demand)/N is demonstrated in the reactor, which establishes the symbiotic balance between the denitrifying sulfur bacteria and sulfate-reduction bacteria [16]. The advantages of autotrophic denitrification include:

– decreasing of the reactor pollution with dead biomass;

– the treated water isn't contaminated with organic carbon.

The implementation of wastewater treatment systems with autotrophic denitrification process use will provide an opportunity to expand the application scope of a number of by-products that currently minimal recycling in traditional industrial processing. For example, the utilization of gaseous sulfur and bio-sulfur.

Figure 9 represents an analysis of the main ecological-trophic groups of microorganisms which take part in autotrophic and heterotrophic denitrification.

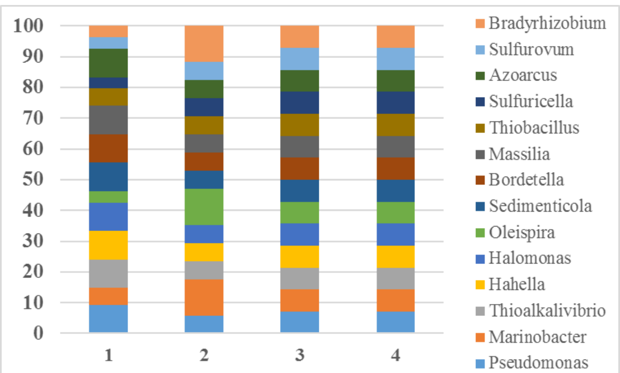

Figure 9 – Taxonomic classification of the microbial composition according to the stages of denitrification: 1 – nitrate to nitrite; 2 – nitrite to nitric oxide; 3 – nitric oxide to nitrous oxide; 4 – nitrous oxide to nitrogen, using KEGG database

The bacterial communities were dominated by Pseudomonas, Bradyrhizobium, followed by Thioalkalivibrio, Thiobacillus, Sulfuricella and Sulfurovum.

Figure 10 presents the data on the metabolic interactions of cooperated communities of microorganisms-denitrifiers in the process of wastewater treatment.

The mechanisms of sulfur conversion in natural ecosystems make it possible to conclude its expediency of use it as a sorption sulfur-containing mineral carrier in wastwater purification systems with further conversion to an organic form (with microbial cell carbonate) (Figure 11).

According to modern conseptualizations, sulfur from surroundings enters the cellular vacuole (filled with voluntarily) of thiobacillus, including T. denitrificans by diffusion and accumulates in it as a reserve material. This sulfur may oxidase as the case should be require. The speed of its oxidation depends on the area of contact of sulfur with bacterial cells. This suggests that there are ferments on the cell area of bacteria that contribute the entry of sulfur into the cell, and under their influence, sulfur is reduced to a sulfide ion, the oxidation of which arises further intracellularly.

Energy and synthesis reactions for an autotrophic denitrification can be written in the form of the following equations.

Energy reaction:

$$2NO_3^- + 5H_2 \rightarrow N_2 + 4H_2O + 2OH^-; \qquad (1)$$

$$2NO_3^- + 2H^+ + 5H_2 \rightarrow N_2 + 4H_2O. \qquad (2)$$

Synthesis reaction [17]:

$$H_2 + 0.35NO_3^- + 0.35H^+ + 0.052CO_2 \rightarrow$$

$$\rightarrow 0.17\ N_2 + 1.1\ H_2O + 0.010C_5H_7O_2N. \qquad (3)$$

The stoichiometric equation for the reduction of nitrate using elemental sulfur proceeds as follows:

$$55S + 20\ CO_2 + 50NO_3^- + 38\ H_2O + 4NH_4^+ \rightarrow$$

$$\rightarrow 4\ C_5H_7O_2N + 25\ N_2 + 55SO_4^{2-} + H. \qquad (4)$$

Heterotrophic denitrification bacteria produce electrons and protons necessary for the transformation of nitrate from organic compounds. These substances include carbohydrates, organic alcohols, amino acids and fatty acids. For example, the utilization of acetate, as a source of carbohydrate, occurs as follows [16]:

$$5CH_3COO^- + 8NO_3- + 3H^+ \rightarrow$$

$$\rightarrow 10HCO_3^- + 4N_2(g) + 4H_2O. \qquad (5)$$

Therefore, developing the denitrification complex technology using gaseous sulfur and bio-sulfur as immobilized sorbing agent for denitrification bacteria followed to technogenic sulfur utilization and fertilizer production.

Thus, it is essential to carry out experimental researches of efficiency of stock package use based on bio-sulfur and gaseous sulfur in biological filters of denitrification systems.

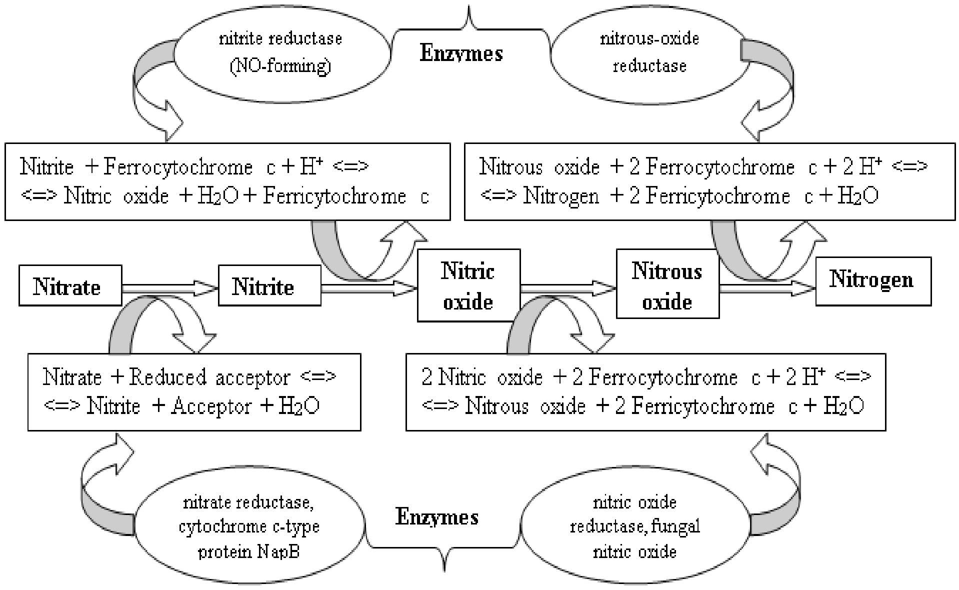

Figure 10 – Block diagram of metabolic processes of interaction in the association of denitrification microorganisms

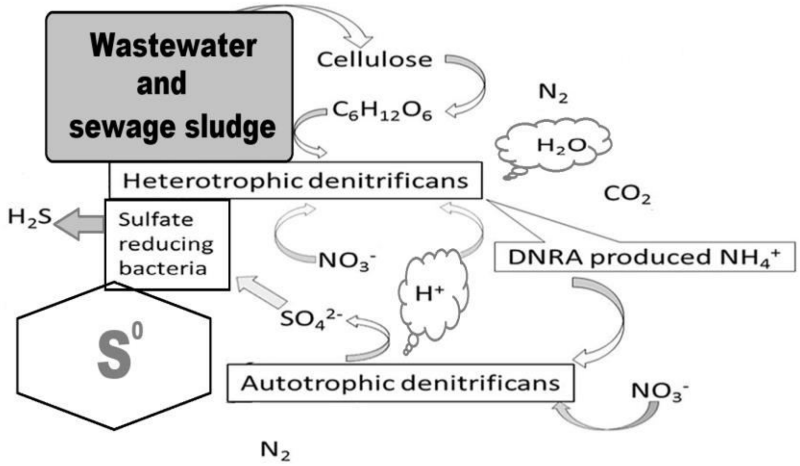

Figure 11 – The flowchart of interactions pathways model in the association of heterotrophic and autotrophic denitrification bacteria in the process of wastewater and sewage sludge purification under condition of elementary sulfur presence

4.2 Bio-filtration set-up system for carrying out the process wastewater denitrification with using bio-sulfur and gaseous sulfur

For pattern drains purification, filtration method is used under anaerobic conditions along with immobilization on the carrier made of autotrophic denitrifying bacterial species such as Thiobacillus denitrificans and Thiomicrospira denitrificans, also usage of phototrophic bacterial species such as Rhodopseudomonas sphaeroides f. denitraficans is possible.

These species will oxidize various kinds of reduced sulfur to sulfate, in this case the nitrate is reduced and oxygen is released for its own metabolism of facultative thiobacteria. Thus, sulfur conversion leads to the reduction of nitrates to nitrites and, ultimately, the release of molecular nitrogen.

Composition of a model contaminated solution: KH_2PO_4, 25 g/dm^3; $MgSO_4{\cdot}7H_2O$, 260 g/dm^3; $KHCO_3$, 753 g/dm^3; $NaNO_2$, 893 g/dm^3; EDTA ($C_{10}H_{16}N_2O_8$), 15 g/dm^3; $FeSO_4$, 5 g/dm^3; $MnCl_2{\cdot}4H_2O$, 0.99 g/dm^3; $ZnSO_4{\cdot}7H_2O$, 0.43 g/dm^3; $CuSO_4{\cdot}2H_2O$, 0.25 g/dm^3.

Figure 12 shows the experimental set-up that is planned to use for wastewater denitrification modelling. The biofilter is a cylindrical container of plexiglass with a volume of 10 dm^3. The reverse flow method is used, in which water is pumped through a hole at the bottom of the filter and ends up, recirculating the water flow through the pump. Also, the gas phase is recycled with the possibility of its recycling into the system to intensify purification process.

In this case, for the implementation of the experiment, the ratio of the main components of the mixture of the filtration material to fill the biofilter is suggested: 2/3 granular sulfur and 1/3 granules (diameter 10 mm) from the calcium-containing material for increasing the pH of the purified water.

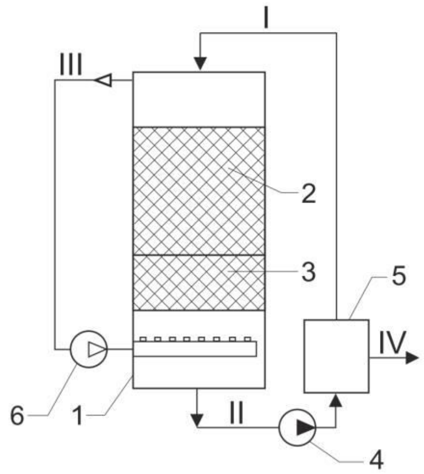

Figure 12 – The bio-filtration set-up system:
1 – biofilter body; 2 – sulfur carrier; 3 – granules of calcium-containing material; 4 – pump; 5 – capacity for selection of model flow; 6 – pump; I – input stream for cleaning; II – output flow for recycling; III – cycle of the gas phase; IV – purified stream

In this case, for the implementation of the experiment, the ratio of the main components of the mixture of the filtration material to fill the biofilter is suggested: 2/3 granular sulfur and 1/3 granules (diameter 10 mm) from the calcium-containing material for increasing the pH of the purified water.

Intensive internal circulation stimulates the growth of the necessary ecological-trophic groups of bacteria, the descending flow of model effluents passes through a layer of granular sulfur and during the bioconversion sulfuric elements of T. denitrificans are used in order to reduce the nitrate to molecular nitrogen. In the process of biochemical conversion, the acid-base balance of the system changes to the acidic side, so a calcium-containing drainage material is loaded in the lower part of the biofilter to buffer the flow of water.

The qualitative character of sulfur use is enlargement of pore spaces inside sulfur-containing granules in the process of sulfur consumption by microorganisms. In 2–3 days after immobilization and beginning of biological filter exploitation, during working presence of essential ecologically-trophic groups of bacteria is exhibited, when gas bubbles begin to form in time intervals between batching of granulated sulfur. It is expected, that in 12–14 days, the durable biofilm with well-developed bacterial intercellular matrix, which covers the whole bulk of sulfur filter medium, is to function. For this purpose, continuous monitoring of the nitrate level in ppm or mg/dm^3 in simulated runoffs before and after purification in the biological filter is conducted.

5 Conclusions

The mechanisms of sulfur conversion in natural ecosystems make it possible to conclude its expediency of use it as a sorption sulfur-containing mineral carrier in wastewater purification systems with further conversion to an organic form (with microbial cell carbonate). The interactions pathways model in the association of heterotrophic and autotrophic denitrification bacteria in the process of wastewater and sewage sludge purification was formed under condition of elementary sulfur presence. Energetic and synthesis reactions for an autotrophic denitrification were described.

Bio-filtration set-up system was formed for carrying out the process wastewater denitrification with using bio-sulfur and gaseous sulfur. The filtration method is used under anaerobic conditions along with immobilization on the sulfur carrier autotrophic denitrifying bacterial species such as Thiobacillus denitrificans and Thiomicrospira denitrificans. These species will oxidize various kinds of reduced sulfur to sulfate, in this case the nitrate is reduced and oxygen is released for its own metabolism of facultative thiobacteria. Thus, sulfur conversion leads to the reduction of nitrates to nitrites and, ultimately, the release of molecular nitrogen.

The implementation of wastewater treatment systems with autotrophic denitrification process use will provide an opportunity to expand the application scope of by-products such as of gaseous sulfur and bio-sulfur that currently minimal recycling in traditional industrial processing.

References

1. Yavorskoy, V. (2016). *Sulfure-gas production in Ukraine*. Lviv Polytechnic National University [in Russian].
2. Dmitriev, E. A., Kuznetsova, I. K., & Akimov, V. V. (2011). *Environmental aspects production sulfuric acid*. Moscow [in Russian].
3. Tsinberg, M. B., & Nenasheva M. N. (2013). Application of gas sulfur in the newest technologies. *Vestnik OGY*, Vol. 10, No. 159, 362–364.
4. Gavrilenko, A. B., Stepacheva, A. A., Molchanov V. P., & Sulman M. G. (2016). Complex denitrification of waste water. *Bulletin science and practice*, Vol. 10, 42–46 [in Russian].
5. Borovykh, E. P. (2011). Denitrification process in biological purification wastewater and calculation methods. *Water chemistry and ecology*, Vol. 11, 85–89 [in Russian].
6. EPA 832-F-07-014 (2007). *Wastewater Management Fact Sheet Denitrifying Filters*. Retrieved from: https://nepis.epa.gov.
7. Thomas, L. (2012). *White Paper Methanol Use in Wastewater Denitrification*. Methanol Institute, USA.
8. *Informatsionnyy byulleten' udaleniya azota*. Retrieved from https://www.ampc.com.au/uploads/cgblog/id338/6.

9. Lampe, D. G., & Zhang, T. C. (1996). *Evaluation of sulfur-based autotrophic denitrification*. Retrieved from https://www.osti.gov/biblio/422853.
10. Ammonium oxidation process and corpulent organic matter wastewater in anthropic anoxic conditions. Certificate of the authorship RU2010125001A (2011). Retrieved from https://patents.google.com/patent/RU2492148C2.
11. Plyatsuk, L. D., & Chernysh, Y. Y. (2016). The removal of hydrogen sulfide in the biodesulfurization system using granulated phosphogypsum. *Eurasian Chemico-Technological Journal*, Vol. 18, No. 1, 47–54.
12. *Biosulfur. Paqell – gas desulpherisation and sulphur recovery with THIOPAQ*. Retrieved from http://www.paqell.com/thiopaq/biosulfur.
13. *Technical sulfur*. Retrieved from http://mnpz.by/products/sera-tekhnicheckaya.
14. Qian, J., Jiang, F., Chui, H. K., Loosdrecht, C. M., & Chen, G. H. (2013). Industrial flue gas desulfurization waste may offer an opportunity to facilitate SANI® application for significant sludge minimization in freshwater wastewater treatment. *Water Science & Technology*, Vol. 67(12), 2822–2826, doi: 10.2166/wst.2013.187.
15. Wu, D., Ekama, G. A., Chui, H. K., et al. (2016) Large-scale demonstration of the sulfate reduction autotrophic denitrification nitrification integrated (SANI®) process in saline sewage treatment. *Water Res.*, Vol. 100, 496–507, doi: 10.1016/j.watres.2016.05.052.
16. *Denitrification in the recycling systems theory and practice* (2016). Retrieved from http://aquavitro.org/2016/01/30/denitrifikaciya-v-recirkulyacionnyx-sistemax-teoriya- i-praktika.
17. Liu, F., Huang, G., & Fallowfield, H. (2014). *Study on heterotrophic-autotrophic denitrification permeable reactive barriers (HAD PRBs) for in situ groundwater remediation*. Springer. Retrieved from http://www.springer.com/978-3-642-38153-9.

Використання сульфуру в біологічних системах біологічної дентріфікації стічних вод

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Анотація. У статті основна увага приділяється вивченню можливості використання мінеральних носіїв з сірки (біо-сірки / елементарної сірки) в системах анаеробного очищення стічних вод в умовах автотрофної денітрифікації. Теоретичні аспекти роботи засновані на біохімічної формалізації процесів очищення з використанням системно-синергетичного підходу для опису закономірностей автотрофних денітрифікуючих мікроорганізмів на основі принципів автокаталізу природних систем. Спеціальне програмне забезпечення використовувалося для визначення необхідних екологічних і трофічних груп мікроорганізмів та для реалізації схем трофічних взаємодій в асоціаціях мікроорганізмів-денітрифікаторів. Таксономічна класифікація призначена на основі бази даних KEGG (Кіотська енциклопедія генів і геномів). Була розроблена система біофільтрації для проведення денітрифікації модельних стічних вод з використанням біо-сірки і газової сірки. Метод фільтрації використовується в анаеробних умовах з іммобілізацією на носії з сірки аутотрофний денітрифікуючих бактеріальних видів Thiobacillus denitrificans і Thiomicrospira denitrificans. Трансформації сірки цими мікроорганізмами призводить до відновлення нітратів до нітритів і до вивільнення молекулярного азоту. Механізми конверсії сірки в природних екосистемах дозволяють зробити висновок про доцільність використання її як сорбційного сірковмісного мінерального носія в системах очищення стічних вод з конверсією в органічну форму (з карбонатом мікробних клітин). Модель шляхів взаємодії в асоціації гетеротрофних і автотрофних денітрифікуючих бактерій у процесі очищення стічних вод і мулових осадів була сформована за умови присутності елементарної сірки. Описано енергетичні реакції і реакції синтезу для автотрофної денітрифікації. Впровадження систем очистки стічних вод з використанням процесу автотрофної денітрифікації дасть змогу розширити сферу застосування ряду побічних продуктів, таких як газоподібна сірка та біо-сірки, які в даний час мінімальні для традиційної промислової переробки.

Ключові слова: денітрифікація, біо-сірка, газова сірка, стічні води, мінеральні носії.