IMPACT OF ETHANOL, METHANOL AND SULFIDES ON THE NITRIFICATION PROCESS OF AMMONIUM IONS IN NATURAL WATERS

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Abstract: This paper includes the results of laboratory modeling of ethyl and methyl alcohol and sulfide ions impact on the biochemical process of ammonium ions nitrification in water from the Dniester River, Palanca village, Stefan Voda district (august 2019). An insignificant influence of ethyl and methyl alcohol (0,5 ml/L) was established in both stages of the process. In the comparison test, the stage $\text{NH}_4^+ \rightarrow \text{NO}_2^-$ lasted 12 days, and in the presence of ethyl alcohol - 14 days and in the presence of methyl alcohol - 16 days. The $\text{NO}_2^- \rightarrow \text{NO}_3^-$ stage in the comparison test lasted 16 days and in the presence of ethyl alcohol 2 days less (14 days) and in the presence of methyl alcohol - 16 days, so without any influence. The study showed a significant influence of sulfur ion in both stages at a concentration of 0.1 mg/L with and without the presence of ethyl and methyl alcohol. In the comparison test, the $\text{NH}_4^+ \rightarrow \text{NO}_2^-$ stage lasted 12 days, in the presence of the S^{2-} ion it lasted 18 days, and in the presence of alcohols and sulfur ion - more than 20 days, the synergism of the impact being obvious. In the $\text{NO}_2^- \rightarrow \text{NO}_3^-$ step of the process for 20 days the NO_2^- concentration did not decrease in the presence of the S^{2-} ion, and in the presence of ethyl, methyl alcohol and S^{2-} only 15-35% of the NO_2^- ions were oxidized, in comparison with the witness test.

1. INTRODUCTION

Inorganic nitrogen compounds (NH_4^+ , NH_3 , NO_2^- , NO_3^-) are present practically in all natural waters, the content of which is conditioned by their amount in existing sources of pollution: wastewater discharged into the environment, the presence of industrial, agricultural, household waste illegally

stored, atmospheric deposits and surface runoff and as a result of their biochemical transformation [3].

As a result of the discharge of wastewater from Chisinau municipality into the water of Bâc river were detected 119 mg/L NH_4^+ , and in Cogâlnic district, downstream of Hâncești city - 24.2 mg/L NH_4^+ [12]. By evaluating the physical-chemical composition of the Bâc river water at the discharge into the Dniester river was found the presence of 32,6-33,8 mg/L of ammonium ions [28].

Ammonium, nitrites and nitrates ions have different toxicity for hydrobionts, and surface waters are classified into 5 quality classes according to their concentration: for nitrates from 1,0 to >11,3 mg N/L; nitrites from 0,01 to >0,3 mg N/L and for ammonium from 0,2 to >3,1 mg N/L [8]. Their presence in water determines the excessive growth of algae causing eutrophication of the aquatic basin [5], and by deteriorating the ecological balance of the aquatic ecosystem; the water quality is also diminished.

Sulfides (S^{2-} , H_2S) are present in wastewater from various economic fields, including domestic, and cause an unpleasant odor already at a concentration of 0,05 mg/L in drinking water [7], but are missing in the list of pollutants to be monitored by the regulation on environmental quality requirements for surface waters [8].

Methyl and ethyl alcohols are also not specified in Government Decision no. 890 of 12.11.2013 [8] and in the Regulation on wastewater collection, treatment and discharge requirements [10], but scientific research has been conducted on their impact on the denitrification process, an example from recent studies of domestic wastewater [2,14] and drinking water [16], being an argument for the purpose of this study of the perpetuation of nitrogen in natural water and, in particular, the oxidation of NH_4^+ ion in the presence of various pollutants present in water: ethanol, methanol and sulfides.

In natural waters ammonium transformations take place through the nitrification process - biological oxidation in two stages: a) with the formation of nitrite ions and b) with the formation of nitrate ions, respectively by Nitrosomonas and Nitrobacter.

The transformation reactions are coupled and take place rapidly until the formation of nitrates, which can be applied to plant growth or the need to remove them from their waters can be reduced by denitrification.

Microbiological processes (nitrification and denitrification) are influenced by temperature, pH, redox potential, the presence of inhibitors and the amount of oxygen in the water.

Nitrification is characterized by high oxygen consumption (for oxidation 1 mg/L of NH_4^+ consumes about 3,6 mg/L O_2), and an insufficient supply of oxygen can lead to the accumulation in water only of nitrites, which leads to creating exceptional situations [6].

Frequent pollution of natural waters with chemicals inhibits the biochemical processes in the environment. Previously has been studied the influence of phenol, petroleum products, heavy metals and pesticides, surfactants, etc., on the process of ammonium nitrification in surface waters [17, 18, 25, 26], because these substances are used in domestic activity in various fields of the economy.

The following paper includes the results obtained by laboratory modeling of the impact of ethyl and methyl alcohols and sulfides in the biochemical process of ammonium ions nitrification in natural water.

2. MATERIALS AND METHODS

The influence of ethyl and methyl alcohols and sulfides on the process of biochemical oxidation of ammonium ions was assessed by determining for 20 days the concentration of NH_4^+ , NO_2^- ions and pH, using national standards [22-24], and NO_3^- ion by the method in the presence of NO_2^- [19].

Figure 1. The map (scheme) of the hydrological basin of Dniester River (Republic of Moldova).

The study of the process was performed using laboratory modeling in glass vessels exposed to sunlight (direct sunlight was excluded). Water was used for the experiment from the Dniester River, Palanca village, Stefan Voda district, Republic of Moldova (fig. 1).

The initial concentration of ammonium ions in water was 0,11 mg/L and was increased to 2,36 mg/L (permissible in urban and industrial wastewater at discharges - 2 mg/L [10]) with ammonium sulfate solution. The comparison sample includes natural water with an NH_4^+ content of 2,36 mg/L. The concentration of ethyl and methyl alcohol was 0,5 ml/L of water, taken at random, because it is not regulated in environmental normative documents. The concentration of sulfides (S^{2-}) in the experiment was taken 0,1 mg/L, 5 times lower than the limited allowable in urban and industrial wastewater at discharges in emission (0,5 mg/L) [10].

Were used chemicals of "pure for analysis" or "chemically pure" quality. The modeling was performed at a temperature of 20-22°C.

3. RESULTS AND DISCUSSIONS

The study of the process of nitrification of ammonium ions is important for river ecosystems and biota present in waters specific to the nitrogen cycle. Nitrification evaluation is also characteristic during aerobic/anaerobic decomposition reactions in wastewater treatment technologies, when nitrogen from organic substances is transformed into inorganic nitrogen compounds toxic to aquatic biota. An example is the information in Council Directive 78/659 / EEC of 18.07.1978 on the permissible concentration of ammonium ions, ammonia and nitrites in water for the maintenance of fish life: salmon waters: $\leq 0,005 \text{ mg/L NH}_3$; $\leq 0,04 \text{ mg/L NH}_4^+$; $\leq 0,01 \text{ mg/L NO}_2^-$; cyprinoid waters: $\leq 0,005 \text{ mg/L NH}_3$; $\leq 0,2 \text{ mg/L NH}_4^+$; $\leq 0,03 \text{ mg/L NO}_2^-$ [4] and limited allowance of 0,5 mg/L NH_4^+ and NO_2^- for drinking water [9].

The influence of ethyl alcohol, methyl alcohol and sulfides on NH_4^+ ion nitrification.

In some studies, some correlations have been proposed that characterize the denitrification process with the use of ethyl and methyl alcohol [13].

Denitrification research into reactors that simulate effluents from domestic wastewater treatment plants using methanol, ethanol and methane as electron donors based on kinetic parameters [20] has shown that the most efficient electron

donor was ethanol, which completely removed nitrogen and nitrates in 50 min, the same efficiency being obtained by feeding the reactors with methanol and methane for 120 and 315 min, respectively. The model is simple and expresses the conversion of nitrate directly to molecular nitrogen.

In some data of the relevant ministry (Ministry of Agriculture and Food Industry, currently the Ministry of Agriculture, Regional Development and Environment) it is specified that 162 licensed economic agents were active in the manufacture, storage and marketing of alcohol production in the Republic of Moldova [28]. For example, during 2016, alcohol production was manufactured in a total volume of 5706.3 thousand liters [1], being used in various fields, some with an impact on the environment, which means that their residues can reach wastewater in the basins.

Methyl alcohol is designed for use in the process of denitrification of wastewater / sludge from Biological Sewage Treatment Plant in Chisinau municipality. The most complex biological treatments include the removal of nitrogen compounds from wastewater. Nitrogen is present in raw domestic wastewater mostly in the form of ammonium (NH_4^+), which is oxidized by autotrophic bacteria to nitrate (NO_3^-) and then reduced by specific bacteria to N_2 under anoxic conditions, the process taking place in the presence of methanol as a carbon source [15]. So, the method is based on improving the activity of denitrifying bacteria, which occur naturally when a slightly degradable organic chemical is added, which the bacteria oxidize and simultaneously reduce the nitrate to nitrogen gas.

Figure 2. The step $\text{NH}_4^+ \rightarrow \text{NO}_2^-$ of the nitrification process in the presence of ethyl and methyl alcohol.

As sulfides (S^{2-} , H_2S) are not included in the list of substances monitored by the Regulation on environmental quality requirements for surface waters [8], but are present in wastewater discharged into the environment, it has been of scientific interest evaluating their impact on the nitrification process in natural waters.

As a result of the evaluation of the process of nitrification of ammonium ions in the water from Dniester River, Palanca village, Ștefan Vodă district (august 2019), an insignificant influence of ethyl and methyl alcohol was established (added in the experiment 0,5 ml/L C_2H_5OH and CH_3OH) in both stages of the process. In the comparison test (control), which includes natural water with the addition of NH_4^+ of 2,36 mg/L, the $NH_4^+ \rightarrow NO_2^-$ step of the nitrification process lasted 12 days, and in the presence of ethyl alcohol by 2 days more (14 days) and in the presence of methyl alcohol - 4 days longer (16 days) (fig. 2).

The $NO_2^- \rightarrow NO_3^-$ step of the nitrification process in the comparison test lasted 16 days, in the presence of ethyl alcohol by 2 days less (14 days) and in the presence of methyl alcohol - 16 days, so without influence (fig. 3).

Figure 3. The step $NO_2^- \rightarrow NO_3^-$ of the nitrification process in the presence of ethanol and methanol.

The study of the ammonium nitrification process shows a significant influence of the sulfide ion on both stages at the concentration of 0,1 mg/L with and without the presence of ethyl and methyl alcohol. If in the comparison test the stage $NH_4^+ \rightarrow NO_2^-$ lasted 12 days, in the presence of the S^{2-} ion it lasted 18 days, and in the presence of alcohols and sulfur ion - more than 20 days (fig. 4), being obviously the synergism of the impact.

Figure 4. The step $\text{NH}_4^+ \rightarrow \text{NO}_2^-$ from the nitrification process in the presence of sulfur ion and ethanol and methanol.

In the $\text{NO}_2^- \rightarrow \text{NO}_3^-$ stage of the nitrification process for 20 days the NO_2^- concentration did not decrease in the presence of the S^{2-} ion and in the presence of ethyl, methyl and S^{2-} alcohol only 15-35% of the NO_2^- ions were oxidized, in comparison with the control sample (fig. 5).

Figure 5. The step $\text{NO}_2^- \rightarrow \text{NO}_3^-$ from the nitrification process in the presence of sulfur ion and ethyl and methyl alcohol.

As a result of the modeling process, the pH of the water decreased from 8,03 to 7,55. The nitrate content increased from 4,6 mg/L to about 13 mg/L in the comparison sample (water from the Dniester River with a concentration of 2,36 mg / L NH_4^+), in the other samples decreasing to about 2,7 mg/L NO_3^- in water with the addition of 0,5 ml/L $\text{C}_2\text{H}_5\text{OH}$ and CH_3OH , the argument may be the denitrification of nitrates in the presence of alcohol.

In the samples with the addition of 0,1 mg/L S^{2-} , including alcohols, the nitrate content did not change substantially and was 3,6-4,1 mg/L, which demonstrates the impact of sulfides on both the nitrification process and denitrification, varying depending on the concentration of alcohol and other pollutants, but also other processes that may occur with HS^- ions, for example [11]:

The process evaluated with HS^- ions demonstrates both the denitrification of nitrates in the acidic environment and the formation of nitrites, sulfur, sulphate and the increase of the acidity of the environment, which confirms the different influence of sulfides on the nitrification process in water.

Because sulfides (S^{2-} , H_2S) are not included in the list of monitored substances in the Regulation on environmental quality requirements for surface waters [8], but, as demonstrated in this paper, have a significant impact on biochemical processes in surface waters and, of course, they must be included in the list of parameters for monitoring and classifying the surface natural water quality.

CONCLUSIONS

The evaluation of ammonium ions nitrification process in water from Dniester River, Palanca village, Ștefan Vodă district, Republic of Moldova, shows an insignificant influence of ethyl and methyl alcohol at a concentration of 0,5 ml/L.

The sulfide ion in both steps of the nitrification process has an obvious impact: in 18 days in the $\text{NO}_2^- \rightarrow \text{NO}_3^-$ stage, only 15-35% of NO_2^- was oxidized, compared to the comparison sample.

As a result of the modeling process the pH of the water decreased from 8,03 to 7,55.

The nitrate concentration increased from 4,6 mg/L to about 13 mg/L in the comparison sample (control), but in the other samples decreasing to about 2,7 mg/L NO_3^- in water with the addition of 0,5 ml/L $\text{C}_2\text{H}_5\text{OH}$ and CH_3OH , the argument may be the denitrification of nitrates in the presence of alcohol.

In the samples with the addition of 0,1 mg/L S^{2-} , including alcohols, the nitrate content did not change substantially and was 3,6-4,1 mg/L, which demonstrates the impact of sulfides on the nitrification process as well as denitrification.

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