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# Impact of Detergents on the Nitrification Process of Ammonium Ions in Natural Waters

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## Abstract

The evaluation of individual effects of surfactants or other ingredients does not reflect the influence of a detergent on the aquatic environment, being important to estimate the effects of detergent as a whole.

The present study, the impact of detergents on the process of nitrification of ammonium ions in natural waters evaluates the influence of 3 types of detergents on the process of nitrification of $NH_4^+$ in water: solid detergents (DS-1 and DS-2) and a liquid detergent (DL). Laboratory modeling evaluated the nitrification process in the water of the Dniester River, in which 2.2-2.5 mg / $dm^3$ $NH_4^+$, 1-10-100 mg / $dm^3$ DS-1 and DS-2 were added and 0.1 -0.5-1.0 ml / $dm^3$ of DL.

The nitrification process (stage I) $NH_4^+ \rightarrow NO_2^-$ in water without detergent (control) took 8 days. At the addition of 1-10 mg/$dm^3$ of DS-1 and DS-2 the process took 9-10 days, and at 100 mg/$dm^3$ - 19-24 days, the concentration of nitrates in stage II ($NO_2^- \rightarrow NO_3^-$) being 19.8-17.2 mg/$dm^3$ for DS -1 and 14.9-1.68 mg/$dm^3$ for DS-2, respectively. The concentration of 0.1 ml / $dm^3$ DL generated the process at stage I to last 19 days, and in the presence of 0.5-1.0 ml/$dm^3$ DL after 30 days there were still 56-88% of the initial ammonium, finally stage II ($NO_2^-NO_3^-$) ending with only 4.67 - 1.01 mg/$dm^3$ of nitrates.

The study confirms the need to assess the impact of detergents (not only surfactants) and wastewater before being discharged into the emissary.

**Keywords**: Ammonium Ions; Contamination of Aquatic Ecosystems; Detergents; Nitrate; Nitrite; Nitrification

## Introduction

In natural waters are present practically all inorganic nitrogen compounds ($NH_4^+$, $NH_3$, $NO_2^-$, $NO_3^-$), 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, surface runoff and as a result of their biochemical transformation [**1**].

The surface waters are divided into 5 quality classes according to the concentration ammonium, nitrites and nitrates ions: 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 [**2**]. Their presence in water determines the excessive growth of algae causing eutrophication of the aquatic basin [**3**], and by deteriorating the ecological balance of the aquatic ecosystem; the water quality is also diminished.

The ammonium ions in waters are important for the nitrification process for the biota present in surface waters and specific to the nitrogen cycle. Process is also characteristic during decomposition reactions in wastewater treatment technologies, when nitrogen from organic substances is transformed into toxic inorganic nitrogen compounds, including $NH_4^+$.

For exemple, as a result of the discharge of wastewater from Chisinau municipality into the water of Bac river were detected 119 mg/L $NH_4^+$, and in Cogalnic district, downstream of Hancesti city – 24,2 mg/L $NH_4^+$ [**4**]. By evaluating the physical-chemical composition of the Bac river water at the discharge into the Dniester river was found the presence of 32,6-33,8 mg/L of ammonium ions [**5**].

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**].

Previously has been studied the influence of phenol, petroleum products, heavy metals, pesticides, surfactants, etc., on the process of ammonium nitrification in surface waters [**7-11**], because these substances are used in domestic activity and in various fields of the economy.

The following paper includes the results obtained by laboratory modeling of the impact of detergent that contained the different type of surfactants, in the biochemical process of ammonium ions nitrification in natural water.

According to European Committee of Surfactants and their Organic Intermediates reports, half of the detergent consumption is used in household applications, and the other half in industries (cosmetics, metal processing, papermaking, leather, etc.). In 2008, it was estimated that more than 4,2 million tonnes of detergents and 1,2 million tonnes of balms were used annually in Eastern Europe, up from 2006 [**12**], the annual global production of surface active agents being about 13 million tons, and 65% are anionic surfactants, the second and third places in the global production correspond to non-ionic and cationic compounds, respectively [**13**].

## Materials and Methods

The conversion of ammonium ions or ammonia into nitrite and respectively in nitrate (oxidation, nitrification) is prods by Nitrosomonas and Nitrobacter aerobic organisms, so the result of study will demonstrate the influence of detergents on the nitrification bacterium.

The influence of detergents on the process of biochemical oxidation of ammonium ions was assessed by determining for 30 days the concentration of $NH_4^+$, $NO_2^-$ and in final $NO_3^-$ ions and pH, using national standards [**14-16**] and $NO_3^-$ ion by the method in the presence of $NO_2^-$ [**17**].

In the present study is evaluating the influence of 3 detergents on the ammonia nitrification process in water: solid detergent DS-1 (5-15% anionic active agents, <5% nonionic active agents, zeolites, enzymes, optical bleaches, fragrance, benzyl benzoate, butylphenyl methylpropional, citronellol, geraniol), DS-2 (5-15% anionic active agents, <5% soap, sodium silicate, 15-30% sodium carbonate ($Na_2CO_3$), optical bleaches, aromatize) and liquid detergent DL (5-15% anionic and cationic active agents, <5% phosphonates, soap, enzymes, benzisothiazolinone, methylisothiazolinone, perfume, alpha-isomethyl ion, citronellol, geraniol).

The nitrification process was evaluated in the water from river Dniester, Palanca village, Stefan Voda district, Republic of Moldova, in which were added of 2,2 - 2,5 mg/dm$^3$ $NH_4^+$ (permissible in urban and industrial wastewater at discharges - 2 mg/L [**18**]).

The initial concentration of $NH_4^+$ in water was of 0,11 mg/L and 2,7 mg/L $NO_3^-$. The comparison sample includes natural water with added 2,36 mg/L of $NH_4^+$. In the models with detergent in experiments was added: 2,2-2,5 mg/dm$^3$ $NH_4^+$, by 1-10-100 mg/dm$^3$ of DS-1 and DS-2 and by 0,1-0,5-1,0 ml/dm$^3$ of DL, using information as a detergent for a wash is about 1 g/L for DS-1, 0,4 g/L for DS-2 and 1,1 ml/L for DL.

In the study were used chemicals of "pure for analysis" or "chemically pure" quality. The modeling was performed at a temperature of 20-22°C and pH of 7,65 in conditions presented by Grunditz C., etc. (2001): optimum temperature is 35°C for Nitrosomonas and 38°C for Nitrobacter; optimum pH is 8.1 for Nitrosomonas and 7,9 for Nitrobacter [**19**].

## Results and Discussions

The European Union adopted in 2004 Regulation 648/2004 on detergents [**20**], which includes the notion of detergent: 'Detergent' means any substance or mixture containing soaps and/or other surfactants intended for washing and cleaning processes. Detergents may be in any form (liquid, powder, paste, bar, cake, moulded piece, shape, etc.) and marketed for or used in household, or institutional or industrial purposes.

So, the detergents used in everyday life are complex mixtures of various compounds. These components can interact antagonistically, additively or synergistically, increasing or diminishing the toxicity of the detergent in the aquatic environment. Thus, evaluating the individual effects of surfactants or other ingredients does not reflect either the actual or net influence of a detergent on the aquatic environment, it is thus necessary to estimate the effects of detergent formulations as a whole [**21, 22**].

In the Regulation (EC) Nr. 648/2004 [**20**] is mention: (7) As confirmed by the Commission White Paper on the strategy for a future Chemical Policy, appropriate measures concerning detergents should ensure a high level of environmental protection, especially of the aquatic environment, so it is important to study the influence of detergents on $NH_4^+$ ion nitrification.

The results of nitrification process evaluated in the water from river Dniester are presented in **figures 1-6**.

The $NH_4^+ \rightarrow NO_2^-$ step in water without detergent (0) lasted 8 days. At the addition of 1-10 mg/dm$^3$ of DS-1 the process took 9 days and at 100 mg/dm$^3$ the duration of the step was 19 (**figure 1**). The $NO_2^- \rightarrow NO_3^-$ step in water without detergent lasted 13 days (0). When adding 1-10 mg/dm$^3$ of DS-1 the process took 13 days and in the presence of 100 mg/dm$^3$ the stage duration was 26 days for DS-1 (**figure 2**).

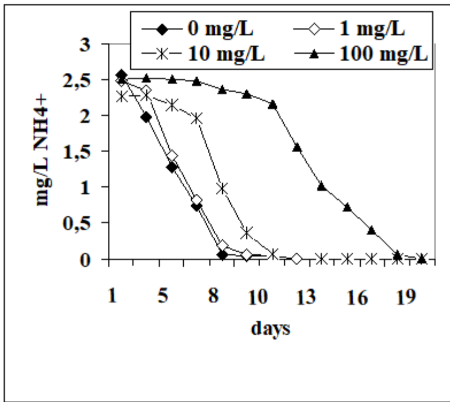


**Figure 1.** The step $NH_4^+ \rightarrow NO_2^-$ in water without detergent (0) and in presence of DS-1 (1-10-100 mg/L).

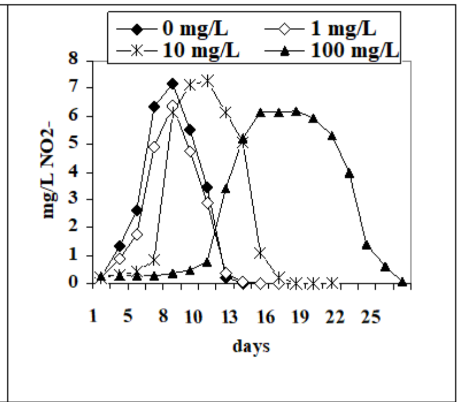


**Figure 2.** The step $NO_2^- \rightarrow NO_3^-$ in water without detergent (0) and in presence of DS-1 (1-10-100 mg/L).

The first stage of the process of nitrification $NH_4^+ \rightarrow NO_2^-$ in water at the addition of 1-10 mg/dm$^3$ of DS-2 the process took 10 days and at 100 mg/dm$^3$ the duration of the step was 24 days (**figure 3**). The $NO_2^- \rightarrow NO_3^-$ step in water when adding 1-10 mg/dm$^3$ of DS-2 the process took 17 days and in the presence of 100 mg/dm$^3$ the stage duration was more than 30 days for DS -2 (**figure 4**).

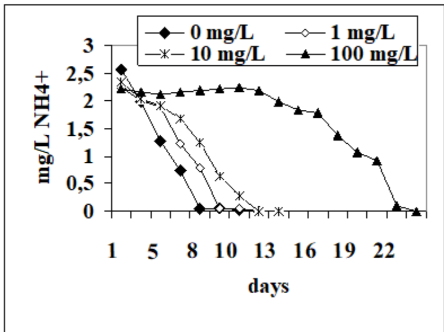


**Figure 3.** The step $NH_4^+ \rightarrow NO_2^-$ in water without detergent (0) and in presence of DS-2 (1-10-100 mg/L).

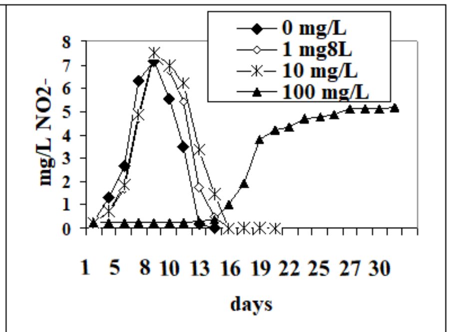


**Figure 4.** The step $NO_2^- \rightarrow NO_3^-$ in water without detergent (0) and in presence of DS-2 (1-10-100 mg/L).

It was shown that at the addition of 0,1 ml/dm$^3$ DL the step lasted 19 days, and in the presence of 0,5-1,0 ml/dm$^3$ after 30 days there were still 56-88% of ammonium ions left (**figure 5**). DL has a specific influence in the second stage of nitrification ($NO_2^- \rightarrow NO_3^-$). At the addition of 0,1 ml/dm$^3$ DL the step lasted 20 days. In the presence of 0,5-1,0 ml/dm$^3$ DL after 30 days in solutions were only 0,63-1,38 mg/dm$^3$ $NO_2^-$ (**figure 6**).

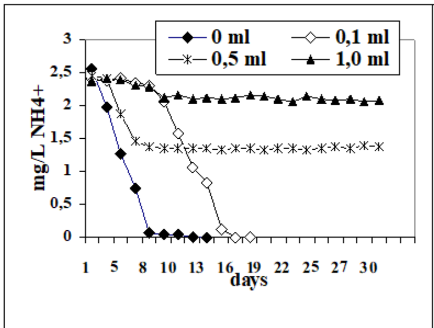


**Figure 5.** The step $NH_4^+ \rightarrow NO_2^-$ in water without detergent (0) and in presence of DL (0,1-0,5-1,0 ml/L).

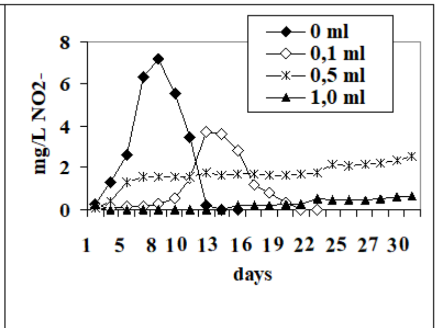


**Figure 6.** The step $NO_2^- \rightarrow NO_3^-$ in water without detergent (0) and in presence of DL (0,1-0,5-1,0 ml/L).

Finally nitrates formed after nitrification in the presence of DS-1 and DS -2 is of 14,6-19,8 mg/dm$^3$, and in water without the addition of detergents – 21,4 mg/dm$^3$ (**table 1**).

DL has a specific influence on the nitrification process. At the addition of 0,1 ml/dm$^3$ DL in final was 14,6 mg/dm$^3$ of nitrates, in the presence of 0,5-1,0 ml/dm$^3$ DL in final being only 4,67-1,01 mg/dm$^3$ of nitrates (**table 1**).

| Water river Nistru | $NH_4^+$, mg/L | Detergent | | $NO_3^-$, mg/L |
|---|---|---|---|---|
| | | Named | Additioned | |
| | 0,11 | | | 2,7 |
| 1 | 2,56 | | 0 | 21,4 |
| 2 | 2,47 | DS-1 | 1 mg/L | 19,8 |
| 3 | 2,26 | | 10 mg/L | 18,4 |
| 4 | 2,51 | | 100 mg/L | 17,2 |
| 5 | 2,23 | DS-2 | 1 mg/L | 14,9 |
| 6 | 2,33 | | 10 mg/L | 17,8 |
| 7 | 2,38 | | 100 mg/L | 1,68 |
| 8 | 2,40 | DL | 0,1 ml/L | 14,6 |
| 9 | 2,46 | | 0,5 ml/L | 4,67 |
| 10 | 2,37 | | 1,0 ml/L | 1,01 |

**Table 1:** The concentration of $NO_3^-$ in water at the end of modeling.

Currently the world production of detergent amounts to 10 millions of tons per years **[23]**. The detergents used are complex mixtures of various compounds that can interact antagonistically, additively or synergistically, increasing or diminishing its toxicity on aquatic biota **[21, 22]**.

The contamination of aquatic ecosystems is increasing at an alarming rate as a consequence of the discharge of untreated sewage of urban and industrial origin into coastal zones, rivers, streams and lakes. Among the contaminants found in these sewage effluents are organic pollutants such as detergents, which can cause toxicity problems for the aquatic biota found in the receiving water bodies **[24]**.

So, is important to study the influence of used detergents on the systems of wastewaters treatment and were wastewater is discharged in the natural waters.

## Conclusions

- In the presence of solid detergents: DS-1 (5-15% anionic active agents, <5% non-ionic active agents, zeolites, enzymes, optical bleaches, perfume, benzyl benzoate, butiphenyl methylpropional, citronellol, geraniol); DS-2 (5-15% anionic active agents, <5% soap, sodium silicate, 15-30% sodium carbonate ($Na_2CO_3$), optical bleaches, aromatized) the content of nitrates ,formed after nitrification is 14.6-19.8 mg/dm$^3$, and in water without the addition of detergents (control sample) is 21.4 mg/dm$^3$.
- DL liquid detergent (5-15% anionic and cationic active agents, <5% phosphonates, soap, enzymes, benzisothiazolinone, methylisothiazolinone, perfume, alpha-isomethyl ion, citronellol, geraniol) has a specific influence on the nitrification process. The concentration of 0.1 ml/dm$^3$ DL in water finally generates an amount of 14.6 mg/dm$^3$ of nitrates, and 0.5-1.0 ml/dm$^3$ only 4.67-1.01 mg/dm$^3$ of nitrates.
- The study confirms the need to assess the impact of detergents (not only surfactants) and wastewater before being discharged into the emissary.

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