INFLUENCES OF ORGANIC AMMONIUM DERIVATIVES ON THE CHANGE OF CONCENTRATIONS OF NH_4^+, NO_2^-, NO_3^- IN RIVER WATER

Petru Spataru

Institute of Chemistry of the Academy of Sciences of Moldova, 3 Academiei, Chisinau, MD-2028, Republic of Moldova, *spatarupetru@yahoo.com*

Abstract

One of the logical reasons for the study of nitrogen is the toxicity of its various forms. Their effect on the natural aquatic environment is very different and depends on the amount and structure of organic radicals associated with amine nitrogen. The difference of the effect of amines of natural origin (diethylamine - DEA) and synthetic origin (1-naphtylamine - 1-NA, diphenylamine - DPA and cetyltrimethylammonium - CTMA) on the processes of ammonia oxidation has been investigated. The maximum allowable concentration (MAC) for synthetic amines and for natural origin amines differs by almost two orders of magnitude. Both natural and synthetic amines affect oxidation-reduction processes caused by the activity of bacterial enzymes, even within MAC values. In the case of 1-NA, the inhibitory effect is associated with a toxic effect, whereas for DEA this effect is doubled (due to a toxic effect, as well as from the amine-bound carbon). CTMA also has an impact on the inhibition of processes. But in the presence of anionic surfactants (egg, lauryl sulfate-LS) in an aqueous medium, the effect of CTMA is clearly reduced. Conversely, the presence of $CaCO_3$ particles reduces the ability of anionic organic substances to decrease the effect of cationic ones. Typically, the amines, arising from the decomposition of organic materials of natural origin, have less toxicity and lower MAC than those of synthetic origin. It is important to note here that laboratory models are sensitive even at concentrations below the MAC. Because of this, MAC can not be perceived as absolute values and only meaning within certain limits.

Keywords: *ammonium, amine, calcium carbonate, nitrite, surfactants*

Introduction

Concerns the behavior of cationic organic substances with different structure and toxicity in surface water, which combine with other types of organic substances, as well as the changes in their combinations in this environment. The amines, which are homologues of the ammonium in which the hydrogen is replaced by various organic radicals and which inhibit the oxidation of ammonium, decompose into the aquatic environment, which complicates the process (Spataru 2011; Britto 2001; Britto & Konzucker 2002; Tanaka 2009). In this situation, the dynamics of the stable, soluble forms (NH_4^+, NO_2^-, NO_3^-) give us new research opportunities (Spataru 2015; Spataru 2017).

In the present study, both amines used in the chemical industry and those that can be the result of natural processes of protein and amino acid decomposition have been investigated. Due to various toxicity, they have maximum admissible concentrations (CMA) ranging for about two orders of magnitude. The study was performed at concentrations below the permissible limit and in case of overdose.

Materials and methods

The model included water samples from the Nistru River, where different amounts of the ammoniacal nitrogen were added. To river water samples, the NH_4Cl solution has been added, in order to achieve concentrations of ~ 3 mg/L and ~ 6 mg/L of ammonium. In parallel with the reference sample, to which only ammonium was added, both amines of chemical industry waste (1-NA, DPA, CTMA) and those resulting from the decomposition of proteins (DEA). Laboratory models have been initiated, respecting the minimum recommended sample of water in glass vessels. The model was produced under natural lighting conditions, away from direct sunlight. Natural water research was conducted according to ISO, the methods published in the literature. Sample testing was performed using the HACH DR/2500 Spectrophotometer.

Results and Discussion

Considering that ammoniacal nitrogen is a physiological product of living organisms eliminated, we can understand its oxidation process in which it participates through its catalytic systems a wide range of bacteria (Müller 2006; Spataru 2011) as one of the reference. Thus, the dynamics of ammonium oxidation can serve as an indicator of the state and potential of self- purifying of the aquatic environment. Laboratory simulations comprised five concentrations (0.025, 0.05, 0.1, 0.25, 0.5) of 1-NA corresponding to 0.5; one; 2; 5; 10 MAC for this one substance.

Dynamics of $[NH_4^+]$; $[NO_2^-]$ in Fig. 1 and Fig. 3 demonstrates the influence of 1-NA on the river water purification process. In previous experiments, the concentration of ammoniacal nitrogen concentration increased by more than 50% of the initial NH_4^+ concentration in the sample with 1-NA after three days of experiment. This increase took about ten days the spring period (Spataru 2015). In the sample containing the same amount (1 MAC) of 1-naphthylamine in the present simulations, we also notice a significant increase in ammonium concentration.
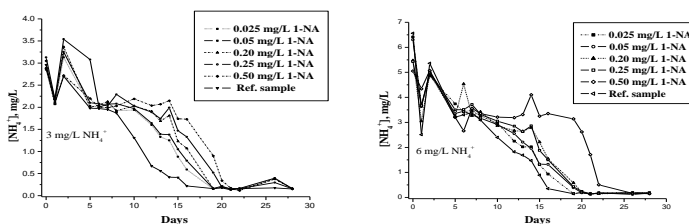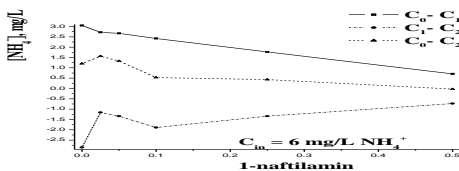

Figure 1. Dynamics of ammonium ions concentration in the Nistru River water containing 3 and 6 mg/L NH_4^+ in the presence of 0.025 mg/L (0.5 MAC); 0.05 mg/L (1.0 MAC;) 0.1 mg/L (2.0 MAC); 0.25 mg/L (5 MAC); 0.5 mg/L (10 MAC) 1-naphtylamine (1-NA)

If microbial populations that have nitrogen fixation properties are well represented, then the selection through the additions introduced into the river water model is possible. This phenomenon is the clearest for 0.05 mg/L of 1-NA and decreasing for 0.25, 0.1 and 0.025 mg/L 1-NA in the presented simulations. The total nitrogen of soluble mineral forms is increasing during the period of nitrogen fixation (on 5 day).

For its 0.5 mg/L, the nitrogen fixation does not take place. Probably, the toxic effect is also dominant for the nitrogen fixation biota. Even at lower and equal concentrations of MAC, ammonium oxidation occurs more difficult than in the reference sample. In the case of concentrations exceeding MAC values of 1-NA, the ammonium oxidation brake is more pronounced. Oxidation braking takes place gradually as the concentration of 1-NA increases.

The changes in the first three days after the initiation of laboratory simulations, in the 6 mg/L NH_4^+ range, the 1-naphthylamine concentration has a well-defined impact. In Figure 2, the trend curves of 1) concentration differences (C_0-C_1) of initiation day and a day after this; 2) the difference between the first and second concentrations (C_1-C_2); 3) that between day of the initiation and after two days (C_0-C_2). By extrapolating the curves of these dependences of 1- NA, we obtain a concentration to which these changes will no longer be. The value of 1-NA, which is supposed to stop these changes completely, is 0.659 mg/L. The synchronization of the increase of the difference value (C_0-C_2) with that of the concentration of total mineral nitrogen in water demonstrates of the possible azotfixation. Denitrification process also brings increasing $[NH_4^+]$. We have to note that the natural aquatic
environment demonstrates obvious sensitivity to the presence of 1-naphthylamine even at concentrations equal to and lower than its MAC. And at the equal and lower concentration than the MAC of the 1-naphthalene, the dynamics of the NH_4^+ and NO_2^- indices describe a similar pathway.

Figure 2. Dynamics of the initial ammonium ion concentration difference on the second and third day in dependence of 1-naphthylamine increase in the laboratory simulations with 6 mg / L NH_4^+

Deviations of the stable soluble mineral form (NH_4^+, NO_2^- și NO_3^-) in water demonstrate a change in the ammonium, nitrite and nitrate ion concentrations due to the oxidation of various forms of organic carbon in the context of nitrate and nitrite oxygen consumption. A decrease in the concentration of nitrite ion at the 20th day is evident in both the 1-NA laboratory simulations of 3 mg/L and of 6 mg/L. Even in the case of the reference sample (with 3 mg/L NH_4^+, without 1-NA), this redox effect is highlighted, which in the ammonium dynamics synchronizes with a small peak. There is an increase in the duration of the intermediate process such as NO_2^- and its concentration. The increase in nitrite takes place simultaneous with developing of heterotrophic and autotrophic bacteria (Spataru 2011).
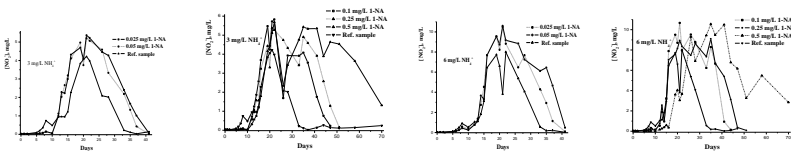
Figure 3. Dynamics of nitrite ions concentration in the Nistru River water with 3 and 6mg/L NH_4^+ and 0.025 mg/L - 0.5 mg/L 1-NA initially

Diethylamine, an amine which is assimilated by aquatic microorganisms, has a more selective toxicity. Even at the MAC value it has the same effect as 1-naphthylamine on redox processes generated by bacterial enzyme activity. The difference between samples of diethylamine simulations compared to 1-NA is manifested by MAC values (almost two orders) for these amines. In the case of 1-NA, only ammonium oxidation is delayed in the model samples containing this amine. And, in the case of diethylamine, there is a delay of both NH_4^+ and nitrite formation exceeds this index compared to the reference sample, braking oxidation and NO_2^- formation and oxidation compared to the reference sample.

The presence of diethylamine (2.0 mg/L) increases the peak value of the ion nitrit formation and oxidation dynamics curve, and in the presence of 20 mg/L DEA, this index decreases in both 3 and 6 mg / L simulations. In the first case, DEA causes an enzymatic activation in which the organic carbon in the river water sample is preferentially involved, but also the organic radicals of the DEA. Decomposition, oxidation, assimilation of DEA occurs naturally much easier than 1-NA. 20 mg/L of DEA in the water sample increases the amount of organic carbon available for reduction. In this case, the dynamics of the redox processes is influenced by both the increased organic carbon (upon addition of 20 mg/L DEA) and the amine nitrogen, which can be converted into the ammonia form. We mention that two steps of increasing ammonium ions are evident. The first period is up to day 5, already described, and the second - only for the sample with 20 mg/L DEA, where the initially massively grows of the ammoniacal nitrogen commensurable with the sum of the added and the one that accumulated on the complete decomposition of this amine.
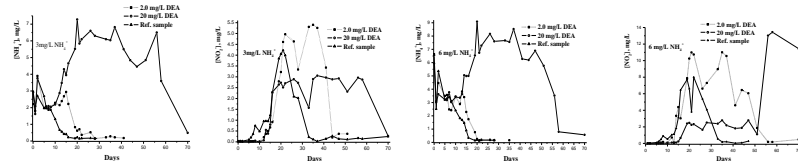
Figure 4. Dynamics of ammonium ions concentration and nitrite in Nistru River water with 3 mg/L and 6 mg/L NH_4^+ and containing 2.0 mg/L (MAC) and 20.0 mg/L (10 MAC) diethylamine (DEA)

The maximum amount of NH_4^+ obtained at the decomposition of 2 mg of DEA is 5.14 mg. For the sample with 20.0 mg/L, the difference between the values of concentrations in days 12-15 and days 20-40 is about 5 mg/L and somewhat longer. In samples with 3 mg/L NH_4^+, there is also a syncronization of the ammonium

concentration maximum with the NO_2^- concentration lows. This aspect denotes a process in which the nitrite nitrogen passes into the ammoniacal one.

Fig. 5 demonstrates the braking of NH_4^+, NO_2^- oxidation in water in both the 1 MAC and even more in those with 10 MAC for DPA samples. Curves of DPA samples are mostly similar to those of 1-NA and will deserve the same comments.
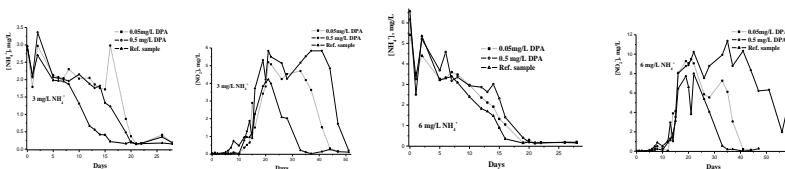
Figure 5. The dynamics of ammonium and nitrite ions (3 mg/L and 6 mg/L NH₄ ⁺ initially) in water Nistru River in the presence of diphenylamine 0.05 mg/L (MAC) and 0.5 mg/L (10 MAC)

In spring samples from the Nistru River, in the presence of $CaCO_3$ the ammonium ion oxidation and formation of nitrite ion is stopped practically. The oxidation of ammonia in the rivulet water of the Cunicea village (Figure 6) is similar in both (in the presence and absence of $CaCO_3$) samples (Spataru 2015). The toxicity of cationic surfactants (SAS) amplifies with the water hardness increasing. The phenomenon of the nitrification braking in the presence of $CaCO_3$ is characteristic for the water of downstream WWTP of cities from where are flows cationic and anionic surfactants in river. In the presence of mixtures of cationic and anionic SAS, the preferential binding of anionic SAS to calcium carbonate particles is found.
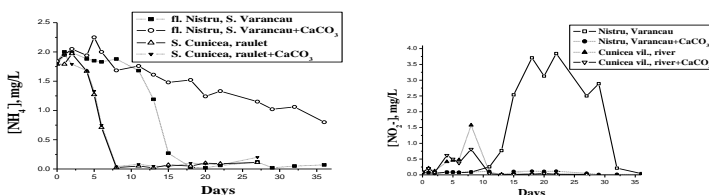

Fig. 6. Dynamics of ammonium (a) and nitrite (b) ion concentration in the waters of the Nistru River, Varancau and in the rivulet of the Cunicea village collected on May 2012

The assessment of these changes was performed using the ability of [Ct SAS*An SAS] complexes to take the form of UV VIS spectrum similar to that of Ct SAS. Thus, the combination [CTMA*LS] has similar spectral line configuration of CTMA (see Fig. 7-a) in the segment of 210-250 nm, but higher values. Using this difference, we can determine the change in concentration of this complex. The study spectra solutions only CTMA (10^{-5} M) and together with LS in the presence of $CaCO_3$ particles, demonstrates considerable changes in aqueous solutions (Fig. 7-c). Thus, the difference spectra movement of complex [CTMA*LS] solution in the absence of $CaCO_3$ particles and in presence of substrate of coincidence with that of only CTMA

solution demonstrates almost complete breakdown of the combination CTMA*LS caused by the presence of $CaCO_3$ nanoparticles. It is necessary to note that in the solution remains SAS Ct. The UV VIS spectra (Fig. 7-c) solution of the CTMA in combination with LS taken in different proportions 1/1 and 1/2 without $CaCO_3$ particles and in their presence, proves the impact of LS of the changes taking place (Spataru 2017). The amount of Ct SAS decreases in solution with increasing An SAS. Thus, the formation of the SAS Kt * SAS An and changes occurring under the impact of calcium carbonate particles is due to geometry, but mostly of hydrophobic chain length of quaternary ammonium species.

In the simulation laboratory research activity, a surface change CaCO3 particles were highlighted difference on UV VIS spectra of aqueous solution of CTMA, with and without NH_4^+. UV VIS spectra of aqueous solutions of cationic SAS do not show the change in concentration to the addition of fine calcium carbonate particles in the absence of NH_4^+ (Fig. 7B). But in the solutions of the CTMA with adding ammonium ion (10^2 mg / L) the change of concentration SAS is evident. Thus, the surface of the calcium carbonate in the absence of ammonium ion is selective of anion SAS only, and adding an aqueous solution of NH_4^+ in the surface of the particles $CaCO_3$ may have the properties of the adsorbent of both the anionic and the cationic SAS. This effect does not depend on the structure of cationic SAS.

| (a) | (b) | (c) |
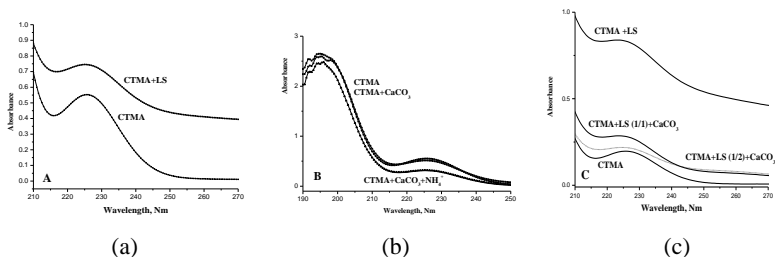
Figure 7. UV VIS spectra (a) of cetiltrimetilamoniului (CTMA) and his combination with lauryl sulfate (LS); (b) of CTMA together with NH_4^+ (10^2 mg/L) and calcium carbonate particle; (c) CTMA solutions in the ratio 1:1 and 1:2 with LS, and the addition of $CaCO_3$

Conclusions

Ammonium derivatives (amines) have a brake impact of redox processes of stable soluble nitrogen forms at concentrations below MAC. With increasing their concentration in river water, the effect is in progress. Calcium carbonate causes no braking nitrification in clean water; Organic cationic pollutants caused in the presence of calcium carbonate produce a clear braking impact on the dynamics of oxidation of NH_4^+, NO_2^- in natural waters. Experience has shown the changes in the SAS interaction with $CaCO_3$ particles, depending on the proportions of these substances in water. So, the transfer and the reorientation of CTMA to carbonate particles takes place depending on the amount of LS. So, decomposition occurs combination CTMA*LS and depositing them on nanoparticles, wherein the first bonding layer is formed with LS, and the rest are oriented based on the hydrophobic chains and groups electrostatic interaction. The UV-VIS method demonstrated the loss of selectivity of calcium carbonate particles is obvious in the presence of higher concentrations (about

10^2 mg/L) of ammonium. Simulations and laboratory tests water samples from the Nistru River demonstrate the Ct SAS negative influence on treatment and self-purification processes.

References
Britto, DT, Siddiqi, MY, Glass, ADM & Kronzucker, HJ 2001, `Futile transmembrane $NH_4^+$ cycling: A cellular hypothesis to explain ammonium toxicity in plants` - *Proceedings of the National Academy of Sciences* USA, pp. 4255–4258.

Müller, T, Walter, B, Wirtz, A & Burkovski, A 2006, `Ammonium Toxicity in Bacteria`, *Current Microbiology*, vol. 52, pp. 400–406.

Sandu, M, Spataru, P, Negru, M, Mosanu, E, Dragutan, D & Goreacioc, T 2007, `The dynamic of nitrification process in the presence of cationic surfactants` - *Proceedings of the International symposium "The Environment and Industry"*, Bucharest, vol. 1, pp. 277-281 (in Romanian).

Spataru, P 2011, *Transformations of organic substances in surface waters of Republic of Moldova*, Ph.D Thesis in Chemistry, State University of Moldova, Chisinau (in Romanian).

Spataru, P, Povar, I, Mosanu, E & Trancalan, A 2015, `Study of stable nitrogen forms in natural surface waters in the presence of mineral substrates` *Chemistry Journal of Moldova*, vol. 10, no.2, pp 26-32.

Spataru, P, Fernandez, F, Sista, JW, Spataru, T, Spinu, O & Povar I 2017, `Influence of the interaction of calcium carbonate particles with surfactants on the degree of water pollution in small rivers`, *Ecological Processes,* vol. 6, no.18, pp.1-8.

Tanaka, T, Hachiyanagi, H, Yamamoto, N, Iijima, T, Kido, Y, Uyeda, M & Takahama, K 2009, `Biodegradation of endocrine-disrupting chemical aniline by microorganisms`, *Journal of Health Science*, vol. 55, no. 4, pp. 625-630.