Behaviour of Nitrogen Soluble Forms in Natural Water in the Presence of Anionic and Cationic Surfactants and Mineral Substrates

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Abstract: The redox processes, organic substances accumulation, chemical equilibria and adsorption of organic substances on the substrate surface function of natural water compositions and substrate granule sizes have been investigated. Laboratory simulations have been carried out for the Nistru and Isnovat river waters. The natural water models containing laurylsulphate (LS) as anionic surfactant (SAS An) and cetyltrimethylammonium (CTMA) as cationic surfactant (SAS Ct), separately and in a body, as well as the substrates $Al(OH)_3$, Al_2O_3, $CaCO_3$, H_2SiO_3, light fraction (clayey) of diatomite and expanded clay powder have been studied. The timely distribution of the soluble nitrogen species containing NH_4^+, NO_2^- and NO_3^- in the samples of natural waters has been analyzed. It has been found that LS diminishes the redox processes braking due to the partial fixation of toxic organic matter. Similar, but more pronounced enhancement impact on oxidation of nitrite ions as a result of fixation and sedimentation of organic components has been found in the case of the calcium carbonate powder. Also, $CaCO_3$ produces a better SAS Ct separation/inactivation of organic part in the presence of both anionic and cationic SASs. A water self-purification processes effectiveness in polluted river waters decreases in the $CaCO_3$, $Al(OH)_3$, Al_2O_3, H_2SiO_3, light fraction (clayey) of diatomite, expanded clay powder substrate series.

Keywords: Cetyltrimethylammonium; Laurylsulfate; Mineral substrates; Nitrogen soluble forms; Surface-active.

1. Introduction

Nitrogen has a wide use in human activity and a significant impact on the environment (soil, water and atmosphere). A useful indicator for estimating water eutrophication is the growth of algae populations, determined by the amount of chlorophyll. The correlation between the total nitrogen content and this indicator can be approximated as a linear [1], but more precisely is a polynomial with a high correlation coefficient. Thus, nitrogen stable soluble species in water generate accumulations of organic matter in the aquatic environment. Nitrites are highly toxic to humans, flora and fauna, being a significant concern regarding water quality [2, 3]. On the other hand, for a wide range of bacteria, in contrast to animal [4] and plant cells [5, 6], ammonia is not toxic, even in molar concentrations due to the fact that, most bacteria prefer ammonia as a nitrogen source. Some species even produce ammonium ion, for instance, N2-fixing Rhizobia Cyanobacteria and Proteolytic Clostridia create ammonia through the fermentation of amino acids. Also it was established that the resistance to ammonia is a common property of bacteria [7]. This allows the use of ammonia and nitrite oxidation process in natural basins water as universal natural effective model of aquatic environment perturbations, in which nitrifying bacteria convert toxic ammonia to lesser harmful nitrate [8]. In water samples, where significant amounts of organic substances and toxic pollutants are present, the inhibition of ammonium oxidation is noticeably [9, 10]. But, ammonium and nitrite ions are easily oxidized by oxygen in river waters in the presence of bacterial enzymes.

The basis of this study was the toxicity of inorganic nitrogen species, in particular the nitrogen reduced forms. Their longer existence is maintained by organic substances that oppose redox reactions in water and those that inhibit the activity of bacterial enzymes [3, 10]. The study of the dynamic processes, which include the stable soluble forms of nitrogen by laboratory simulations demonstrates diminishing braking effect of nitrification processes in the Nistru River waters, caused by the decreasing of the cationic surfactants toxicity in the presence of anionic ones [11, 12]. However, these starting data are not enough for drawing the appropriate conclusions regarding their practical use and implementation. More detailed studies are necessary for a complete understanding of the nitrogen species behavior, including the toxic ones in natural basins water. The main aim of this paper is the investigation of the influence of $CaCO_3$, $Al(OH)_3$, Al_2O_3, H_2SiO_3, light fraction (clayey) of diatomite and expanded

clay powder substrates and their granule size on the redox processes of soluble nitrogen forms in the presence of the anionic (LS) and cationic (CTMA) SAS.

2. Experimental part

The most part of laboratory simulations have been carried out during 2015-2017 years for less polluted waters of the Nistru River and more polluted ones of the Isnovat River (the affluent of the Bac River, a tributary of the Nistru River). A smaller number of water samples were taken from other rivers of the Republic of Moldova (see the map, Fig.1). The tests of natural waters were accomplished according to ISO methods [13-18]. Laboratory trials were carried out in glass vessels, respecting the minimum recommended water-sample model volume (3 L). Keeping the same volume and conditions for the whole series of samples used for laboratory simulations is essential (Sandu et al. 2007). The initial ammonium ion concentration of 2 mg/L was obtained by adding $(NH4)_2SO_4$ or NH_4Cl to each sample. The purity of all used substances corresponded to ISO [13-18 requirements. The surfactant's (*LS, CTMA*) purity was at least equal to 98.5%. Natural water samples, containing separately *LS* as anionic surfactant (*SAS An*) and *CTMA* as a cationic surfactant (*SAS Ct*) and their mixture as well as the substrates $Al(OH)_3$, Al_2O_3, $CaCO_3$, H_2SiO_3, light fraction (clayey) of diatomite and expanded clay powder, have been investigated. The surfactant concentration below 10^{-5} mol/L was used to avoid the micelle formation. The analysis of the soluble nitrogen-containing compounds (NH_4^+, NO_2^- NO_3^-) behavior in the samples of natural water and their modeling were performed according to standard ISO methods [13-18] at the same time of the day [19]. Laboratory simulations were accomplished under the static conditions. Stirring was carried out after each series of tests. The analysis of samples was done using a HACH DR/2500 spectrophotometer using Perkin Elmer Lambda 25 and LOMO SF-46.
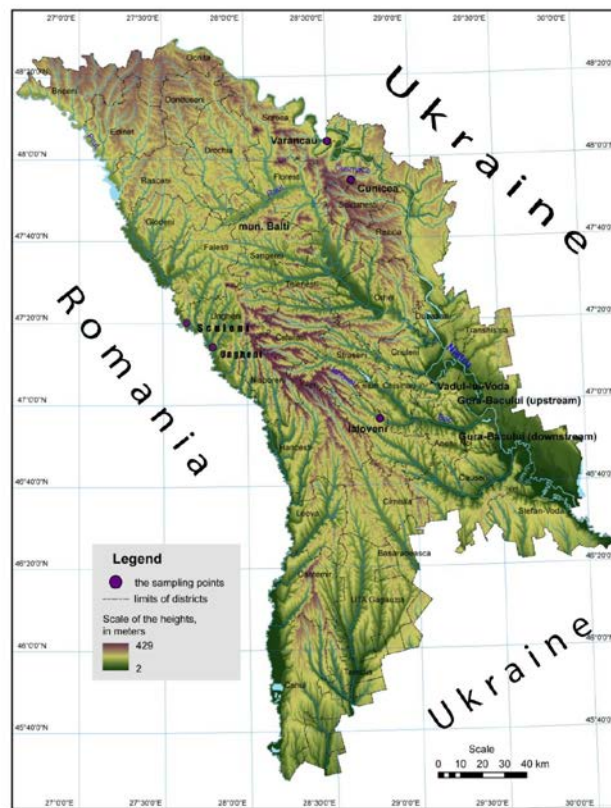

Fig. 1. Map of the Republic of Moldova

3. Results and discussion

The curves presenting the formation and oxidation of NO_2^- have as similar shape as curves of decomposition and oxidation of organic matter in waters collected from a number of rivers sections (Fig. 2, b). It is worthy to note, that the concentrations of nitrite ions in the same samples are mainly proportional to each other, reflecting similar processes for rivers waters.
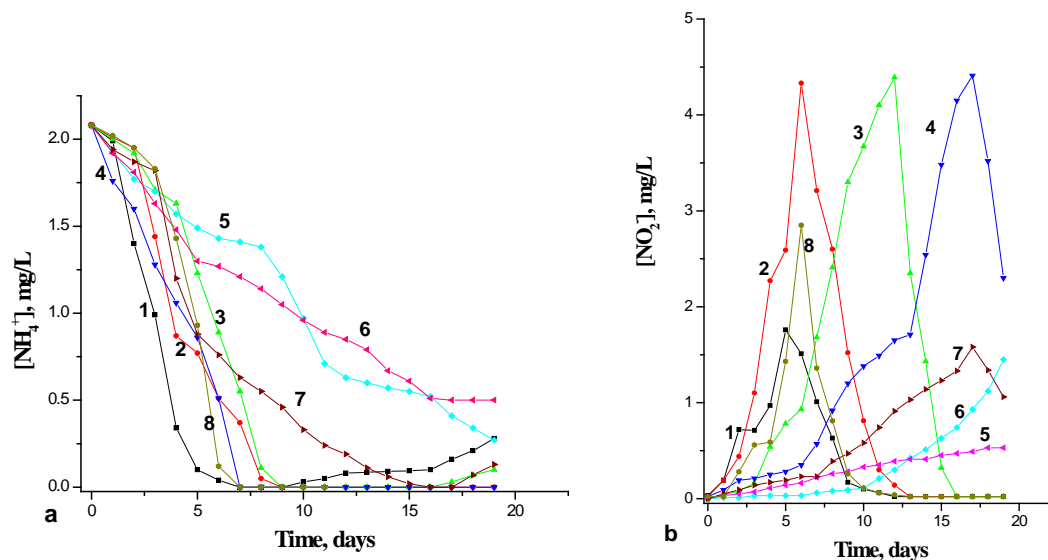
Fig. 2. The dynamics of ammonium *(a)* and nitrite *(b)* ion concentration (the same initially added ammonium ion ammount) in different rivers 1 (Raut, Baraboi), 2 (Cubolta, Gribova), 3 (Nistru, Meresauca), 4 (Ciuhur, Ocnita), 5 (Racovat, Hodarauti), 6 (Racovat, Corestauti), 7 (Racovat, Halahora de Jos), 8 (Hlinoaia, Lake)

The established sensitivity of this ion to organic matter and water-soluble oxygen explains the specificity of each sample taken from rivers water [3, 10]. Obviously, the dynamics of ammonium concentration changes (with the same initial $[NH_4^+]$ ammount) in waters of different rivers proves, that due to the different composition, each sample of water manifests its particularity (Fig. 2, a).

In the samples taken for water simulations from the Nistru River, the *SAS An*: *SAS Ct* = 5:1 ratio was kept matching both surfactant maximum admissible concentrations in natural waters [10]. In these simulations of the *SAS An* adding, the braking effect of nitrification processes in the Nistru River causes the decrease of the *SAS Ct* toxicity. On the other hand, *SAS An* and *SAS Ct* separately and together are characterized by the similar dynamics ammonium and nitrite ions concentration modifications in polluted waters of the Isnovat River [20].

It has been shown, that for surfactant concentrations above 10^{-5} mol/L, the formation of micelles in the surfactant mixture takes place [12]. It was found that the dynamics of $[NH_4^+]$ and $[NO_2^-]$ is changing in the Isnovat River after massive rains becomes more complex, since pesticides and other toxic compounds are washed from the soils in the rivers waters. LS binds to other organic compounds from river waters facilitating the oxidation of above mentioned nitrogen forms. In water, which contains other cationic organic components than those added in our simulations, the *SAS An · SAS Ct* combination does not show the brake diminution of self-purification processes.

The initial molar ratio *LS : CTMA* was kept of 1:1 in the samples from the Isnovat River polluted waters, because of pronounced bracking effect. Both *SAS Ct* separately and with *SAS An* of the 1:1 ratio inhibits the purification process, because a part of anionic surfactant is bound in other, more stable combinations. As a result, the *SAS Ct* toxicity does not change significantly. The expected effects after the addition of surfactants in river waters depend on previously formed and accumulated organic compounds [20]. The presence of *LS* in river waters fixes and masks the inhibition properties of organic matter and, therefore, perturbs or inhibits completely the redox processes. The Nistru River, downstream of the Soroca city (Section Varancau), constitutes a source of pollution by sewage. The presence of cationic detergents may explain the difference between the samples in the presence of calcium carbonate [21]. In the sample containing $CaCO_3$, the ammonium ion oxidation is stopped completely (Fig. 3 and 4). The same figures show also the dynamics of the concentration modifications in NH_4^+ and NO_2^- ions for the river of Cunicea at Cunicea village which water does not contain synthetic surfactants. The oxidation of ammonia in this river water is similar in with and without calcium carbonate samples. Water samples of the Nistru River at the Bursuc village river are less polluted in comparison to the Varancau ones, but their pollution degree is still noticeable (Fig. 3).

The inhibition effect is registered in the Nistru River (Bursuc section) samples with $CaCO_3$, but it is less than in the Varancau section of the Nistru River. The water from the Sculeni section of the Prut River (sampled in summer) was less polluted (Fig. 3), than downstream of WWTP of the Ungheni city, where water was more polluted, therefore, with larger braking effect. The $CaCO_3$ added in the samples of Nistru, Varancau and Prut, Ungheni after WWTP, is completely blocking the nitrification process [21]. On the other hand, the toxicity of cationic surfactants increases with increasing water hardness [11, 12]. Both these factors, the presence of $CaCO_3$

and increasing water hardness, effects can explained if one admits the complex [*anionic SAS · cationic SAS*] formation, which decomposes after its adsorption to the surface of calcium solid phases. In the presence of mixtures of cationic and anionic surfactants, the preferential binding of anionic surfactants to calcium carbonate particles has been found [22-24]. After the filling out of first layer by anionic surfactants on the substrate surface, the deposition of both the [*anionic SAS · cationic SAS*] complex and *SAS An* takes place on the subsequent layers. Both calcium carbonate and calcium ion fix the anionic fraction of organic matter in water. The cationic part of organic matter, as well as *SAS Ct*, becomes unbounded, so the oxidation inhibitory action for ammonium and nitrite ions increases. The sedimentation of suspended particle of the $CaCO_3$ substrate can rapidly alter the course of self-purification processes.
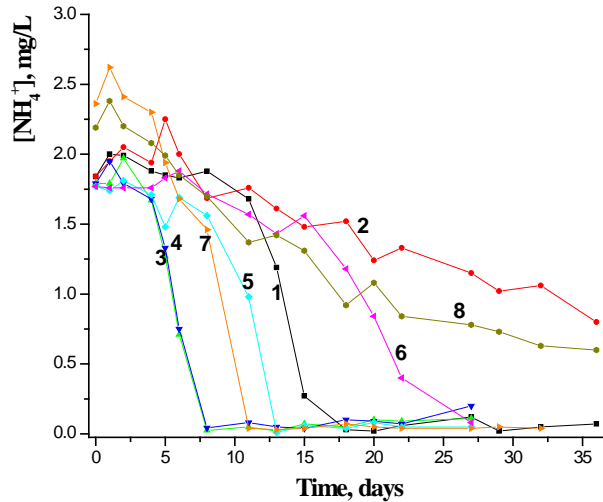

Fig. 3. The dynamics of ammonium ion oxidation within laboratory simulations with the initial concentrations of 2 mg/L NH_4^+ in river waters: 1 (Nistru, Varancau), 2 (Nistru, Varancau + $CaCO_3$), 3 (v. Cunicea, river), 4 (v. Cunicea, river + $CaCO_3$), 5 (Nistru, Bursuc), 6 (Nistru, Bursuc + $CaCO_3$), 7 (Prut, Ungheni, after WWTP), 8 (Prut, Ungheni, after WWTP + $CaCO_3$)
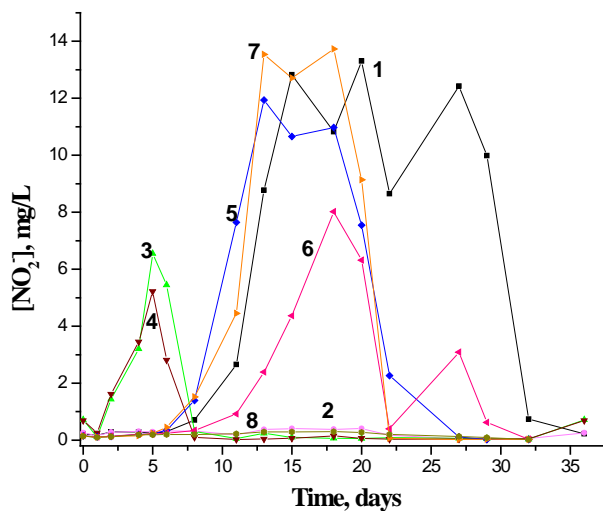

Fig. 4. The dynamic of nitrite ions concentration modifications within laboratory simulations with the initial concentrations of 2 mg/L NH_4^+ in river waters: 1 (Nistru, Varancau), 2 (Nistru, Varancau + $CaCO_3$), 3 (v. Cunicea, river), 4 (v. Cunicea, river + $CaCO_3$), 5 (Prut, Sculeni), 6 (Prut, Sculeni + $CaCO_3$), 7 (Prut, Ungheni, after WWTP), 8 (Prut, Ungheni, after WWTP + $CaCO_3$)

The UV VIS spectra [20] of the clear centrifuged solutions of *CTMA* with *LS* in ratios 1:1 and 1:2 with and without $CaCO_3$ prove the existence of the *SAS An · SAS Ct* complex in the aqueous solution. The complex is formed in comparatively small quantities coexisting with the free *SAS Ct* at the ratio *SAS An* : *SAS Ct* of 1:1 when

$CaCO_3$ is added. The free *SAS Ct* does not exist for the ratio *SAS An : SAS Ct* of 2:1 in the presence of $CaCO_3$, while there is a small amount of complex in clear aqueous solutions. The *SAS Ct* concentration in the solution evidently depends on the *SAS An* concentration in water samples. Adsorption of *SAS Ct* and *SAS An* mixtures on the surface of calcium carbonate substrate can be used as for decontamination of water polluted with cationic surfactants. Oxidation of nitrite ions demonstrates also that, certainly, $CaCO_3$ facilitates the redox process by the better fixation and sedimentation of organic components in natural waters within laboratory simulations (Fig. 4, V. Cunicea river and Fig. 5 *b*).
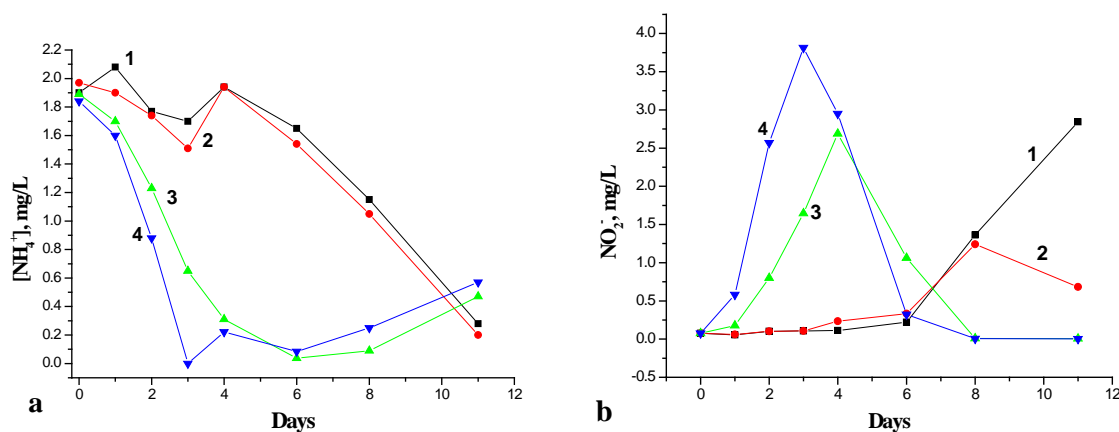

Fig. 5. Dynamics of ammonium (*a*) and nitrite (*b*) ions concentration modifications in the water from the Isnovat River (Ialoveni town) with the initial concentrations of 2 mg/L NH_4^+ 1- reference sample, 2 - in the presence of $CaCO_3$, 3 - granite and 4 - expanded clay with the size of particles from 5 to 0.2 mm

The presence of 0.2-5 mm granite and expanded clay substrates granule amplifies the oxidation of ammonia and nitrites compared to the reference samples and to the samples containing $CaCO_3$. One can observe in Fig. 5, that the influence of calcium carbonate on the oxidation of nitrogen forms is more pronounced in the case of NO_2^-. This can be explained by the fixation of a part of organic matter from natural waters, acting likewise as a reducing agent.

A special role in the processes of self-purification of natural waters plays the nature of organic matter and its quantity. In the laboratory simulations (Fig. 6) with water samples of the Isnovat River, the organic matter prevails at least by two orders the quantities of *SAS Ct* (*CTMA*). At the same time, the most organic matter in rivers is of anionic type [10]. In this case, the augmentation of the oxidation process in the presence of calcium carbonate is noticeable for both ammonium and nitrite ions. It is highly possible that cationic surfactants are deposited on the calcium carbonate particles through the anionic part of organic matter in river waters. This association mechanism of cationic and anionic surfactants is analogous to that described in [22-24]. Hypothetically, the deposition of organic matter on the calcium carbonate particles occurs through its anionic moiety. Then a layer of the anionic organic substance mixture in combination with the cationic one (including *CTMA*) is formed. The newly formed particles are less hydrophilic and can more easily coagulate and precipitate. The formation of relative small amounts of nitrite ions in the presence of $CaCO_3$ can serve as an indicator of the mentioned mechanisms similarity. Since the studied light clay surface particles are charged negatively, the *SAS Ct* (*CTMA*) is deposited directly on this substrate surface. Figure 6 shows that *CTMA* and added substrate cause a decrease in the surfactant inhibitory property. *CTMA* is expected to accumulate completely on the substrate surface. The light clay is mainly composed of montmorillonite and its surface is in general well hydrated and dispersed [25, 26]. *CTMA* does not cause its significant dehydration [27, 28], being accumulated on the substrate surface. Consequently, the association of *CTMA* and light clay surface particles in the suspended form assures a partial maintenance of the surfactant inhibitory properties. In the case of the H_2SiO_3, the substrate surface is charged less negatively and the decrease of the inhibitory properties is lower, because of its weak dissociation. One can observe from the Fig.6 that in the case of H_2SiO_3 the maximum concentration of nitrite ion is lower comparing to the light clay. A decrease in the ammonium oxidation rate and an acceleration of nitrite ion oxidation processes are observed from the same figure. The delay (compared to H_2SiO_3) of oxidation of ammonium and nitrite at the highest maximum NO_2^- concentration takes place in the presence of suspended expanded clay particles. Al_2O_3 and $Al(OH)_3$ exhibit the lowest influence on diminishing the inhibitory effect. The $Al(OH)_3$ substrate, with a positive (at pH=7-8) and potentially fragmented surface, has the most damaging impact on the bracking oxidation processes of nitrogen forms in aquatic environment. Fig. 6 shows that in the absence of anionic surfactants the deposition of *CTMA* on

the light clayey fraction of diatomite, H_2SiO_3, expanded clay, Al_2O_3 and $Al(OH)_3$ substrates is less efficient than its deposition on $CaCO_3$.
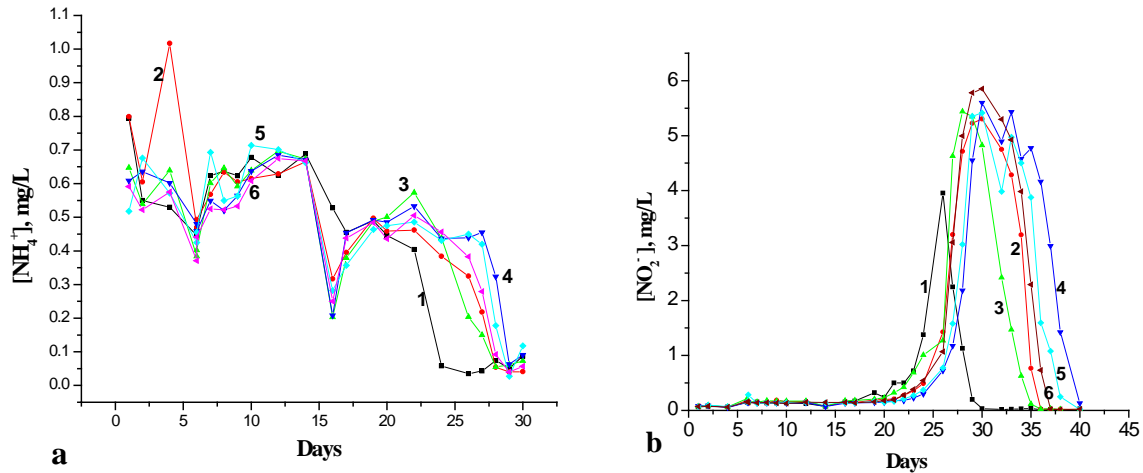

Fig. 6. Dynamics of ammonium (*a*) and nitrites (*b*) ions concentration modifications in waters of the Isnovat River (in the Ialoveni town) in the presence of *CTMA* and the substrates: $CaCO_3$ (**1**), $H2SiO_3$ (**2**), clayey light fraction of diatomite (**3**), $Al(OH)_3$ (**4**), Al_2O_3 (**5**), and expanded clay powder (**6**)

Fig. 7 shows that $CaCO_3$ assures the best cationic separation/storage of organic substances in the presence of both anionic and cationic *SASs*. For samples, containing both *SAS Ct* and *SAS An*, the degree of oxidation of nitrogen soluble forms decreases in the $CaCO_3$, H_2SiO_3, light fraction (clayey fraction) of diatomite, $Al(OH)_3$, Al_2O_3 and expanded clay powder series of substrates. The influence of substrates on the oxidation of both ammonium and nitrite ions is the same in the samples containing each substrate separately. According to the UV spectra [20], the removal of organic matter from waters, polluted through land rainwater washing, is considered. Thus, in the present of $CaCO_3$ particles together with *SAS An* and *SAS Ct*, a significant amounts of water-soluble organic matter are deposited (together with *SAS*) on the carbonate particles surface. One can observe in Fig. 7 that in the samples containing three substrates: $CaCO_3$, H_2SiO_3 and light dolomite fraction, the ammonium ion oxidation rate values are close. On the other hand, the differences in dynamics of nitrite ion concentration changes for these samples are noticeable.

The acceleration of formation and especially oxidation of NO_2^- in the laboratory simulations (samples with $CaCO_3$) sustains the hypothesis that can be a coagulation phenomenon of the calcium carbonate particles, which leads to changes in the activity of *SAS* fixed on the surface of this mineral substrate. The reduction in toxicity of *CTMA* is bigger in samples containing the anionic *SAS*. Consequently, it is possible to understand the phenomenon of capture of cationic components through the formation of *STA Ct · STA An* complexes on the surface of the suspended carbonate particles.

In the model samples containing both *SAS Ct* and *SAS An*, in addition to H_2SiO_3, a lesser degree of the *SAS Ct* removal, but much better than with *CTMA* only, is registered. The light diatomite fraction occupies third place in the first group according to the oxidation rates of nitrites. Generally, as one can see from Fig. 6 and 7, the increase of the ammonium and nitrite ion oxidation rates in the presence of both *SAS* types (*CTMA* and *LS*) is bigger than for the model containing *CTMA* only.

In the samples containing Al_2O_3, $Al(OH)_3$ and expanded clay the substrate particles are retained for a long time in suspended form, generating an inhibition effect on water purification processes (Fig 7a). Fig. 6 and 7 show that the braking effects take up to forty days and it results that *LS* to *CTMA* does not practically change the inhibition action of *CTMA* in the presence of expanded clay substrate. Expanded clay particles have a similar density with water and are practically suspended. The braking effect is the highest for the dynamics of NO_2^- concentration behavior for all the substrates in samples containing both *CTMA* and *LS*. For the expanded clay particles of 5-0.2 mm size, the braking effect is opposite, stimulating the oxidation process of both ammonium and nitrite ions (Fig. 5). So, in this case, the most differences can be related to the size of the substrate granules.

The presence of anionic *SAS* improves self-cleaning process in samples in the following series of substrates: $CaCO_3 \gg H_2SiO_3 >$ clay fraction $> Al_2O_3 > Al(OH)_3 >$ expanded clay.
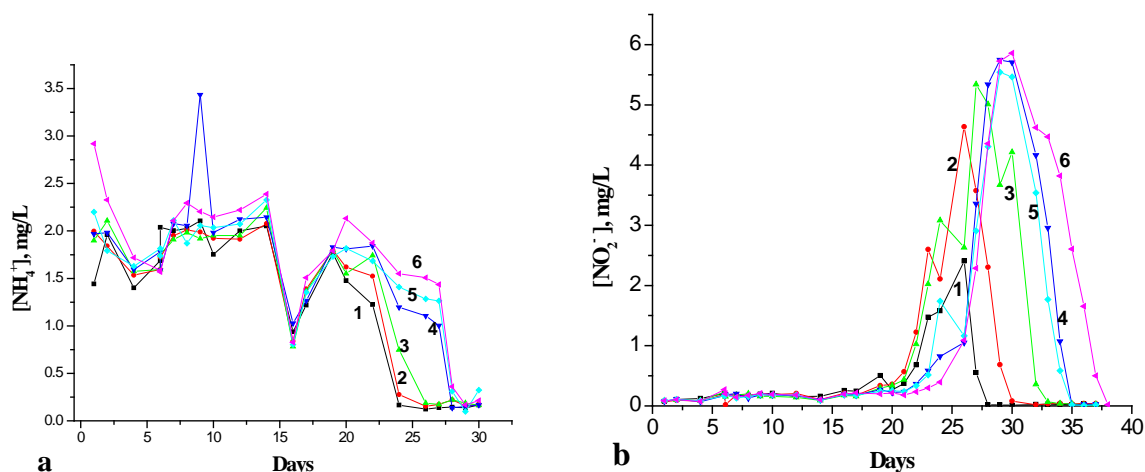
Fig. 7. Dynamics of ammonium (*a*) and nitrites ions (*b*) concentration modifications in the water of the Isnovat River (the Ialoveni town) in the presence of *CTMA, LS* and the substrates: *CaCO₃* (**1**), *H₂SiO₃* (**2**), clayey light fraction of diatomite (**3**), *Al(OH)₃* (**4**), *Al₂O₃* (**5**), and expanded clay powder (**6**)

4. Conclusions

The effect of *LS* presence consists in fixation and masking of a part of the river water organic matter that brakes the oxidation of nitrogen reduced forms. The rate of nitrification processes is higher in the samples containing both *CaCO₃* and the anionic *SAS*. Therefore, calcium carbonate powder contributes to the acceleration of oxidation of toxic nitrite ions, improving the natural water quality. *CaCO₃* facilitates the redox processes by fixation and sedimentation of organic components. In addition, calcium carbonate causes the best cationic separation in the presence of both anionic and cationic *SASs*. The degree of water self-purification in the rivers water with cationic surfactants decreases in the presence of cationic and anionic surfactants in the following series of mineral substrates: $CaCO_3 \gg H_2SiO_3 >$ light fraction (clayey fraction) of diatomite $> Al_2O_3 > Al(OH)_3 >$ expanded clay powder. The sensitivity of the environment to activity of substrate modifications is expected to be dependent on the nanoparticle size of their granules. An increase in the substrate particle size decreases the rates of self-purification process braking by the accumulation of harmful organic component on their surface.

5. References

[1]   Phillips G, Pietiläinen OP, Carvalho L, Solimini A, Solheim AL, Cardoso AC. Chlorophyll–nutrient relationships of different lake types using a large European dataset. Aquatic Ecology. 2008;42(2):213-226.
[2]   Nowka B, Daims H, Spieck E. Comparison of oxidation kinetics of nitrite-oxidizing bacteria: Nitrite availability as a key factor in niche differentiation. Appl Environ Microbiol. 2015; 81(2): 745-753.
[3]   Philip S, Laanbroek HJ, Verstraete W. Origin, causes and effects of increased nitrite concentrations in aquatic environments. Rev. Environ Sci Biotechnol. 2002; 1: 115-141.
[4]   Martinelle K, Haggstrom L. Mechanisms of ammonia and ammonium ion toxicity in animal cells: Transport across cell membranes. J Biotechnol. 1993; 30: 339–350.
[5]   Britto DT, Siddiqi MY, Glass ADM, Kronzucker HJ. Futile transmembrane NH₄⁺ cycling: A cellular hypothesis to explain ammonium toxicity in plants. Proceedings of the National Academy of Sciences of USA. 2001; 98: 4255–4258.
[6]   Britto DT, Konzucker HJ. NH₄⁺ toxicity in higher plants: a critical review. J. Plant Physiol. 2002; 159: 567–584.
[7]   Müller T, Walter B, Wirtz A, Burkovski A. Ammonium toxicity in bacteria. Curr Microbiol. 2006; 52: 400–406.
[8]   Sandu M, Spataru P, Arapu T, Lupascu T. Biochemical oxidation – a pathway for ammonia removal from aquatic systems. NATO Science Series Volume: Methods and Techniques for Cleaning-up Contaminated Sites, ESP. 982358. 2007. p. 142-146.
[9]   Mosanu E, Spataru P, Lupascu T, Sandu M, Goreacioc T, Tarita A. The evolution of biochemical oxidation of ammonia ions in small rivers water. Chem J Mold. 2010; 5(1): 78-83.

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

[11] Lewis MA. Chronic toxicities of surfactants and detergent builders to algae: A review and risk assessment. Ecotoxicol. Environ. Saf. 1990; 20: 123-140.

[12] Lewis MA. The effects of mixtures and other environmental modifying factors on the toxicities of surfactants to freshwater and marine life. Water Res. 1992; 26 (8): 1013–1023.

[13] Coquery M, Morin A, Becue A, Lepot B. Priority substances of the European Water Framework Directive: analytical challenges in monitoring water quality. TrAC Trends in Analytical Chemistry. 2005;24(2):117-127.

[14] ISO 5667-6:2014. Preview water quality - sampling - Part 6: Guidance on sampling of rivers and streams.

[15] ISO 11732:2005. Water quality - Determination of ammonium nitrogen - Method by flow analysis (CFA and FIA) and spectrometric detection.

[16] ISO 8466-1:1990. Water quality - Calibration and evaluation of analytical methods and estimation of performance characteristics - Part 1: Statistical evaluation of the linear calibration function.

[17] ISO 13395:1996. Water quality — Determination of nitrite nitrogen and nitrate nitrogen and the sum of both by flow analysis (CFA and FIA) and spectrometric detection.

[18] Sandu M, Lupascu T, Tarita A, Goreacioc T, Turcan S, Mosanu E. Methods for nitrate determination in water in the presence of nitrite. Chem. J. Mold. 2014; 9: 8-13.

[19] Bernal S, Merbt SN, Ribot M, Casamayor EO, Martí E. Day–night ammonium oxidation in an urban stream: the influence of irradiance on ammonia oxidizers. Freshwater Science. 2017;36(2):272-283.

[20] Spataru P, Fernandez F, Sista JW , Spataru T , Spinu O, Povar I. Influence of the interaction of calcium carbonate particles with surfactants on the degree of water pollution in small rivers. Ecol Process. 2017; 6:18.

[21] Spataru P, Povar I, Mosanu E, Trancalan A.   Study of stable nitrogen forms in natural surface waters in the presence of mineral substrates. Chem J Mold. 2015; 10: 26-32.

[22] Cui ZG, Cui YZ, Cui CF, Chen Z, Binks BP. Aqueous foams stabilized by in situ surface activation of $CaCO_3$ nanoparticles via adsorption of anionic surfactant. Langmuir. 2010; 26 (15): 12567–12574.

[23] Cui ZG, Cui CF, Zhu Y, Binks BP. Multiple phase inversion of emulsions stabilized by in situ surface activation of CaCO3 nanoparticles via adsorption of fatty acids. Langmuir. 2011; 28(1): 314–320.

[24] Cui. ZG., Li W, Qi JJ, Wang HJ. Individual and mixed adsorption of alkylcarboxylbetaines and fatty amide ethoxylates at Daqing sandstone/water interface. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2012; 414: 180–189.

[25] Fu M, Zhang Z, Wu L, Zhuang G, Zhang S, Yuan J, Liao L. Investigation on the co-modification process of montmorillonite by anionic and cationic surfactants. Applied Clay Science. 2016;132:694-701.

[26] LI Feng-qi Preparation of the organic montmorillonite with different surfactants. Appl Chem Ind Engineering. 2008; 04.

[27] Atkin R, Craig VSJ, Biggs S. Adsorption kinetics and structural arrangements of cationic surfactants on silica surfaces. Langmuir. 2000; 16: 9374-9380.

[28] Smith JA, Tuck DM, Jaffe PR, Mueller RT. Organic Substance and Sediments in Water, Backer R, Ed. Chelsea, MI, USA: Lewis Publishers; 1991.p. 201.