

## Controlled nitrification in wastewater treatment

E N Burnashova<sup>1,2</sup>, S Yu Semyonov<sup>2</sup> and A K Sibataev<sup>2</sup>

<sup>1</sup>Siberian Research Institute of Agriculture and Peat – branch of the Siberian Federal Science

Centre of Agrobiotechnologies, 3 Gagarina str., Tomsk 634050 Russian Federation

<sup>2</sup>Tomsk State University, 36 Lenina Avenue., Tomsk 634050 Russian Federation

E-mail: lichtgestalte@mail.ru

**Abstract.** In the present study we investigated a method of controlled nitrification. The technique may significantly reduce the cost of wastewater treatment. The obtained results confirmed the effectiveness of the proposed method. To carry out laboratory studies of the nitrification process, a mineral medium was used in tap water, the ammonium ion concentration was 31 mg / l. It was established that the maximum ammonium removal efficiency is 95-99% with a minimum level of the 48 cm bend of the siphon, with an increase in the level to 153 cm- decreases to 44-57%. The results of measuring the concentration of nitrates show that with the increase in the level of the siphon knee, the formation of nitrates in wastewater is reduced. The maximum concentration of nitrates is formed at a minimum level of the siphon knee 48 cm and is  $101.29 \pm 2.4$  mg / l, with an increase in the level to 153 cm - decreases to  $53.89 \pm 5.7$  mg / l. During the experiments it was revealed that the "Tidal-flow" technology in combination with the siphon discharge of treated effluents allows to control the degree of ammonium nitrification by changing the position of the siphon knee. Two variants of realization of controlled nitrification for automation of the process are proposed.

### 1. Introduction

At present, one of the most important areas of environmental protection is the prevention of pollution of natural reservoirs by substances of the nitrogen group [1-6], the sources of which are sewage from livestock enterprises, domestic sewage and sewage from a number of industrial enterprises. The discharge of such wastewater into natural bodies of water has a toxic effect on hydrobionts [7-9]. One of the stages of wastewater treatment from nitrogen pollution is the process of nitrification, the result of which is the conversion of ammonium ions to nitrate and nitrite ions. Ammonium is more than 20 times more toxic for hydrobionts than nitrate ion. Therefore, even with the complete absence of the denitrification stage in a particular technology, nitrification can reduce the multiplicity of exceeding the MAC (maximum allowable concentrations) for nitrogen pollution from 5.8 or more times. At the same time, the degree of transformation of ammonium to concentrations below the MAC is not only not necessary, but even harmful, because while in the waste water the content of the most toxic form of nitrogen, the nitrite ion (MAC<sub>px</sub> for nitrogen - 0.02 mg / l) is often increased [10]. Thus, in the practice of wastewater treatment, there is a need for structures and methods for controlled nitrification, which optimize the treatment of wastewater by the ratio of ammonium nitrate. In systems with activated sludge, such technologies are known. There are no such solutions for biofilters. Controlled nitrification is a key step in the implementation and the most advanced technology of anaerobic ammonium oxidation (ANAMMOX), including in systems "constructed wetlands" [11-14]. At this stage, the goal is to achieve an equality of molar concentrations of ammonium ions and nitrite ions.

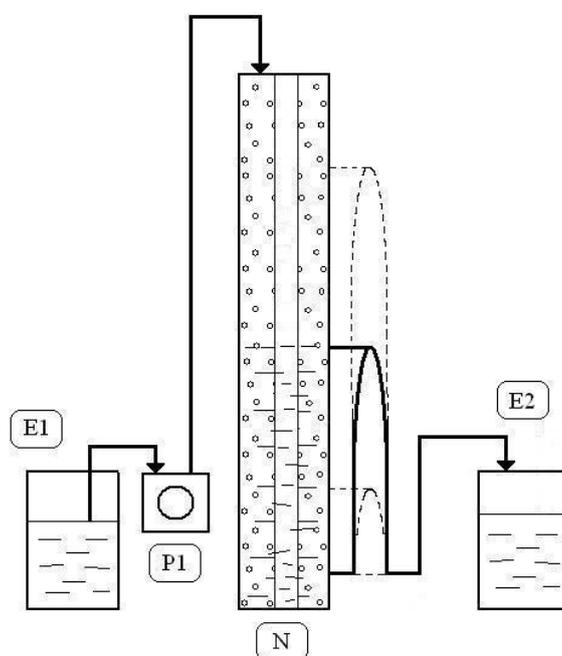


The aim of the work is to develop a controlled nitrification method in biofilters and a device for its implementation.

## 2. Experimental part

### 2.1. Materials

The laboratory fermenter (Figure 1), which manages nitrification, is a plastic cylindrical container with a diameter of 10 cm and a height of 1.75 m. A plastic perforated tube with a diameter of 2 cm is located inside the nitrifying reactor, which allows monitoring the level of the bioreactor filling with effluent, ammonium ion concentration, nitrates, dissolved oxygen. Capacities are divided between a layer of gravel fraction of 5-20 mm. The working volume of the bioreactor is 5.7 liters, the wastewater is supplied by a peristaltic pump «WATSON-MARLOW 502S» through silicone tubing from the top downward at a rate of 1 l / h. To carry out laboratory studies of the nitrification process, a mineral medium was used in tap water, which consisted of  $(\text{NH}_4)_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ , the ammonium ion concentration was 31 mg / l.



**Figure 1.** Scheme of the nitrification reactor (E1, E2 - tanks for raw and treated effluents; P1 - peristaltic pump; N - reactor for the realization of the nitrification process).

The biofilm was built up in the reactor with nitrifying bacteria for twelve weeks in the regime of a conventional biofilter with recirculation of effluent to achieve a 97-percent transformation of ammonium into oxidized forms of nitrogen. During the cultivation of microorganisms nitrifying bacteria of the first and second stages of the genus *Nitrosomonas* and *Nitrobacter* were found.

### 2.2. Research Methods

Photometric and ionometric methods for determining the concentration of the ammonium ion and nitrates were used to control the purification efficiency.

Daily photometric measurement of the concentration of ammonium and nitrates using a spectrophotometer Spekol 1300 by Analytik Jena AG, Germany was performed in an accredited laboratory of the Siberian Research Institute of Agriculture and Peat, a branch of the Federal State Budgetary Institution of Science of the Siberian Federal Research Center for Agrobiotechnology of the Russian Academy of Sciences (SibNIISKhT - branch of the Russian Academy of Sciences). The

following methods were used to measure the mass concentration of ammonium and nitrate ion ions: Method for measuring the mass concentration of nitrate ions in drinking, surface natural and waste waters by the photometric method with salicylic acid (PND F 14.1: 2: 4.4-95) edition 2011, measurements of the mass concentration of ammonium ions in natural and waste waters by the photometric method with the Nessler reagent (PND F 14.1: 2.1-95) edition 2004.

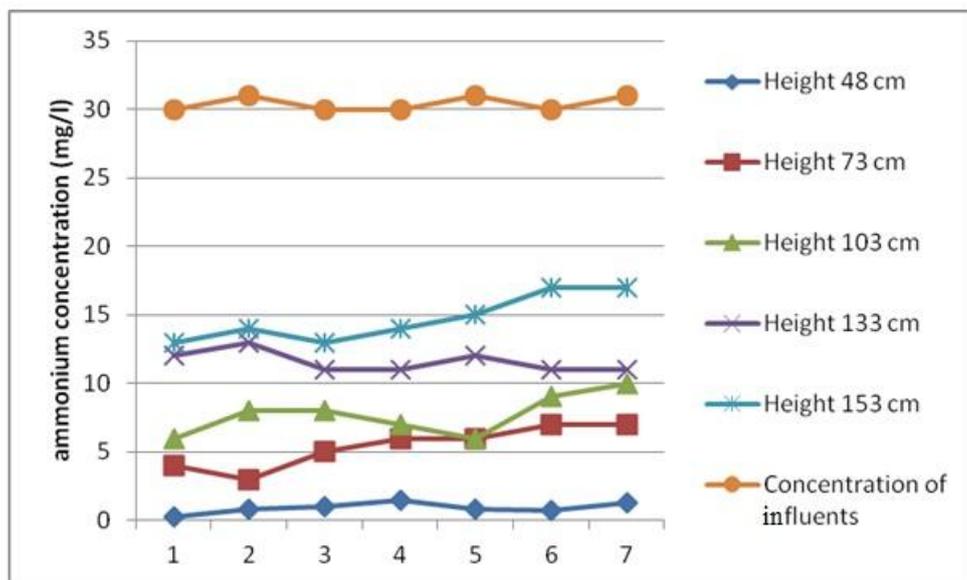
Ionselective electrodes ELIS-121  $\text{NH}_4$ , ELIS-121  $\text{NO}_3$ , a measuring analyzer of liquid MULTYTEST IPL-513 and a system of ion-selective electrodes for measuring ammonium and nitrate nitrogen ISEmax CAM40 / CAS40 were used as a control of the clock dynamics of the changes in the concentrations of ammonium and nitrate ions.

Mathematical processing of measurement results was carried out using Microsoft Office Excel 2007.

### 3. Results and discussion

In an experimental study, the dependence of the degree of ammonium oxidation on the level of filling of the reactor with sewage was studied using periodic flooding and effluent discharges (tidal-flow system, [15-17]) in the bioreactor performing the nitrification process. The position of the siphon knee determines the exposure time of the effluents in the bioreactor, as well as the contact time and the surface area of the filtering charge, on which the biofilm that is in contact with atmospheric air is immobilized (Figure 1). The operation of the siphon for discharge with the maximum filling of the biofilter with wastewater causes the lowest degree of nitrification, and vice versa, the inclusion of a siphon with the minimum filling of the reactor with effluent ensures the greatest efficiency of the transformation of ammonium into oxidized forms of nitrogen.

The measurements were made at 5 different positions of the siphon knee (48, 73, 103, 133, 153 cm from the bottom, 8 cm from the bottom being a "dead zone") to detect changes in the dynamics of ammonium and nitrate concentrations.



**Figure 2.** Dependence of the concentration of ammonium (mg / l) on the position of the siphon.

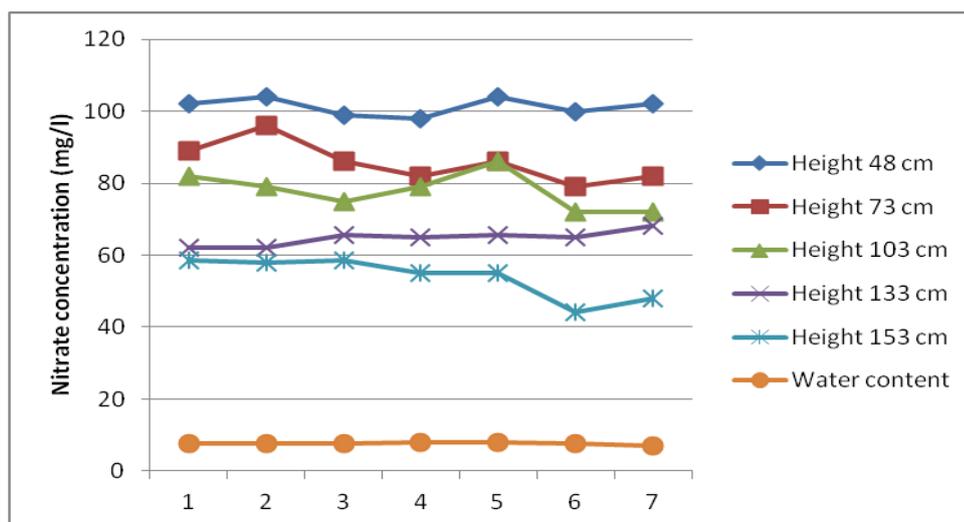
The results of ammonium concentration change experiments show (Figure 2) that with an increase in the level of the siphon knee, the oxidative power is expected to decrease.

**Table 1.** The average concentration of ammonium (mg / l) in wastewater after purification in a nitrifier reactor at different positions of the siphon.

Position of the siphon knee, (cm)	Average concentration, (mg / l)	Removal efficiency, (%)
48	0.9±0.4	95-99
73	5.4±1.5	77-90
103	7.7±1.5	67-80
133	11.6±0.8	57-63
153	14.7±1.7	44-57

It was found that the maximum efficiency of removal of ammonium is 95-99% (Figure 2, Table 1) with a minimum level of the siphon tip of 48 cm, with an increase in the level to 153 cm - is reduced to 44-57%. The average concentration of ammonium ions varies from  $0.91 \pm 0.4$  to  $14.71 \pm 1.7$  mg / l.

The results of measuring the concentration of nitrates (Figure 3, Table 2) show that with the increase in the level of the siphon, the formation of nitrates in wastewater is reduced. It was found that the maximum concentration of nitrates is formed at a minimum level of the 48 cm bend of the siphon and is  $101.29 \pm 2.4$  mg / l, with an increase in the level to 153 cm, it decreases to  $53.89 \pm 5.7$  mg / l.

**Figure 3.** Dependence of nitrate content (mg / l) on the siphon knee position.**Table 2.** The average concentration of nitrates (mg / l) in the wastewater after purification in the nitrifier reactor at different positions of the siphon

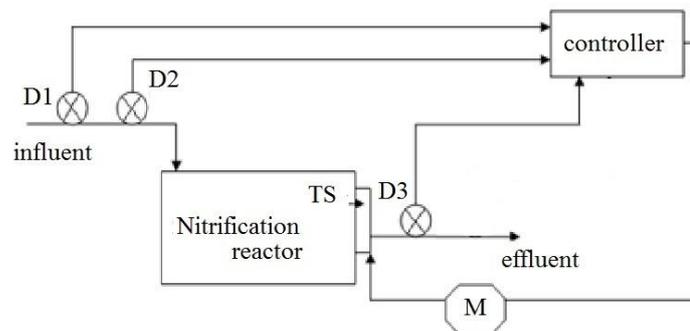
Position of the siphon knee, (cm)	Average concentration, (mg / l)
48	101.3±2.4
73	85.7±5.6
103	77.9±5.2
133	64.7±2.1
153	53.9±5.7

The recalculation of the concentrations of ammonium and nitrate ions by their concentration with respect to nitrogen shows practically a complete balance of the nitrogen process. With a lowering of

the level of the siphon knee from maximum to minimum, the concentration of ammonium in the treated effluents varied from 23 mgN / l to 11 mgN / l, and the concentration of nitrates from 11 to 23 mgN / l, which indicates the absence of the denitrification process in the reactor, as expected in Experiment, because In the model sinks there is no organic matter necessary for denitrification. It is obvious that with a longer process flow in the system, autochthonous organic matter is formed from the biomass of nitrifiers and signs of denitrification will appear.

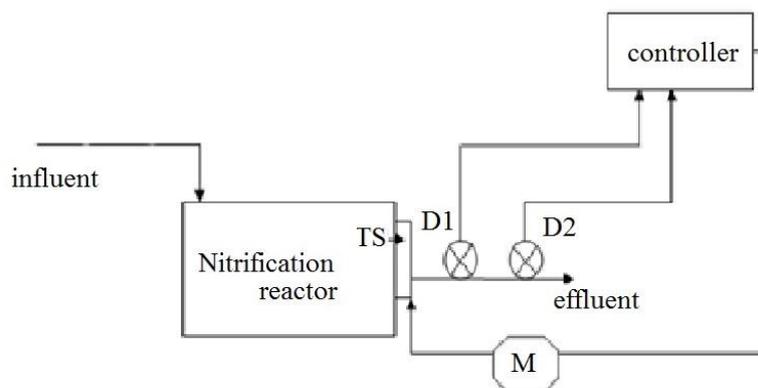
To implement the technology of controlled nitrification, for example, the following two algorithms can be used:

1. Since the oxidizing power must be proportional to the amount of ammonium that is supplied, it is necessary to recalculate the input concentrations by the mass of ammonium entering the reactor (mg / h). In order to do this, it is necessary to have at the entrance to the system 2 sensors: an ionomer for determining ammonium and a flowmeter. At the output, only an ionomer is needed. The position of the siphon knee changes (rises or falls) in two cases - if the amount of ammonia entering the reactor increases, and if the ammonium concentration at the outlet does not meet the control objective (Figure 4).



**Figure 4.** Scheme No. 1 of the controlled nitrifying reactor (Note: D1 - the flowmeter; D2, D3 - ionomer ( $\text{NH}_4^+$ ); M - servo of the position of the siphon knee; TS - the elbow of the siphon).

2. If an anammox-process is used after the controlled nitrifikator for wastewater treatment, you will need to use sensors to determine the ammonium and nitrate concentrations only at the outlet. If the concentration of ammonium over nitrogen is greater than that of nitrites, the siphon knee is lowered and vice versa (Figure 5).



**Figure 5.** Scheme No. 2 of the controlled nitrifying reactor (Note: D1 - ionomer ( $\text{NO}_3^-$ ); D2 - ionomer ( $\text{NH}_4^+$ ); M - servo of the position of the siphon knee; TS - the elbow of the siphon).

#### 4. Conclusions

During the experiments it was revealed that the "tidal-flow" technology in combination with the controlled siphon discharge of treated effluents allows to control the degree of ammonium nitrification by changing the position of the siphon knee. If the specified efficiency of nitrification is exceeded, the siphon tip should be raised, and if it is not effective, lower it. It was found that the maximum efficiency of removal of ammonium is 95-99% with a minimum level of the siphon 48 cm, with an increase in the level to 153 cm - is reduced to 44-57%. The results of measuring the concentration of nitrates show that with the increase in the level of the siphon knee, the formation of nitrates in wastewater is reduced. The maximum concentration of nitrates is formed at a minimum level of the siphon knee 48 cm and is  $101.29 \pm 2.4$  mg / l, with an increase in the level to 153 cm - decreases to  $53.89 \pm 5.7$  mg / l. Such a control algorithm can be automated using a simple control system including ammonium ion concentration (electrode) concentration sensors and water flow at the reactor inlet and a stepper motor raising (lowering) the rod on which the bend of the siphon is secured.

#### Acknowledgens

The work was supported by the "Science Foundation of D. I. Mendeleev" of Tomsk State University. Registration number of the research: No. 8.1.17.2017

#### References

- [1] Fudala-Ksiazek S, Luczkiewicz A, Fitobor K and Olanczuk-Neyman K 2014 Nitrogen removal via the nitrite pathway during wastewater co-treatment with ammonia-rich landfill leachates in a sequencing batch reactor *Environ Sci Pollut Res Int* vol 12 pp 7307-18
- [2] Soliman M and Eldyasti A 2016 Development of partial nitrification as a first step of nitrite shunt process in a Sequential Batch Reactor (SBR) using Ammonium Oxidizing Bacteria (AOB) controlled by mixing regime *Bioresour Technol* vol 221 pp 85-95
- [3] Wei D, Zhang K, Ngo H H, Guo W, Wang S, Li J, Han F, Du B and Wei Q 2017 Nitrogen removal via nitrite in a partial nitrification sequencing batch biofilm reactor treating high strength ammonia wastewater and its greenhouse gas emission *Bioresour Technol* vol 230 pp 49-55
- [4] Yao Q and Peng D 2017 Nitrite oxidizing bacteria (NOB) dominating in nitrifying community in full-scale biological nutrient removal wastewater treatment plants *AMB Express* vol 1 p 25
- [5] Burnashova E N, Martynov M S and Semenov S Yu 2015 Microbiological methods of wastewater treatment from nitrogen compounds *Achievements of science and technology of agroindustrial complex* **29** (2) 49-52 (In Russian)
- [6] Burnashova E N and Semenov S Yu 2016 Influence of physicochemical factors on ANAMMOX-process *Achievements of science and technology of agroindustrial complex* **30** (5) 78-81 (In Russian)
- [7] Wall S M 1996 Ammonium transport and the role of the Na,K-ATPase *Miner Electrolyte Metab* vol 22(5-6) pp 311-7
- [8] Martinelle K and Häggström L 1993 Mechanisms of ammonia and ammonium ion toxicity in animal cells: transport across cell membranes *J Biotechnol* **3** 339-50
- [9] Trukhina A I 2011 Optimization of the Deamox process and molecular biological studies of emerging consortia of microorganisms *PHD Diss.* (In Russian)
- [10] Dua R D and Bhandari Band Nicholas DG D 1979 Stable isotope studies in the oxidation of ammonia to hydroxylamine by *Nitrosomonas europaea* *FEBS Lett.* vol 106 pp 401-4
- [11] Ciudad G, Rubilar O, Munoz P, Ruiz G, Chamy R, Vergara C and Jeison D 2005 Partial nitrification of high ammonia concentration wastewater as a part of a shortcut biological nitrogen removal process *Proc. Biochem.* vol 40 (5) pp 1715-9

- [12] Ruiz G, Jeison D, Rubilar O, Ciudad G and Chamy R 2006 Nitrification-denitrification via nitrite accumulation for nitrogen removal from wastewaters *Biores. Tech.* vol 97 (2) pp 330–5
- [13] Zeqin Dong and Tieheng Sun 2007 A potential new process for improving nitrogen removal in constructed wetlands - Promoting coexistence of partial-nitrification and ANAMMOX *Ecological engineering* **31** 69–78
- [14] Kalyuzhnyi S, Gladchenko M, Mulder A and Versprille B 2007 Comparison of quasi steady state performance of the DEAMOX process under intermittent and continuous feeding and different nitrogen loading rates *Biotechnol. J.* **2** 894–900
- [15] Austin D, Lohan E and Verson E 2003 Nitrification and denitrification in a Tidal vertical Flow wetland pilot *Proceedings of the Water Environment Technical Conference*
- [16] Sun G, Gray K R, Biddlestone A J and Cooper D G 1999 Treatment of Agricultural Wastewater in a Combined Tidal Flow-Downflow Reed Bed System *Wat. Sci. Tech.* vol 40(3) pp 139–146
- [17] Mc Bride G and Tanner C 2000 Modeling biofilm nitrogen transformation in constructed wetland mesocosms with fluctuating water levels *Ecological Engineering* **14** 93–106