INCREASES IN REMOVAL OF PHOSPHORUS COMPOUNDS DURING BIOLOGICAL TREATMENT OF URBAN WASTEWATER IN CONSTRUCTIONS WITHOUT ZONING

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ABSTRACT

Indicators of biological treatment of urban wastewater from the compounds of nutrients (nitrogen and phosphorus) during processing in aeration tanks (aerotanks) without zoning of the traditional scheme «primary clarifier aerotank secondary settling tank» were studied. Research was carried out at the existing wastewater treatment plants of Kharkov and in laboratory experiments. It was established that the concentration of nutrients in the incoming wastewater to the treatment plant exceeds the admissible concentration. Treatment processes in the studied plants include ammonification and nitrification, while the denitrification process does not occur. The concentration of mineral nitrogen compounds in the effluent, as a rule, does not exceed the regulatory limits at Kharkov's biological wastewater treatment plant. The concentration of phosphate in wastewater after the secondary settling tank exceeds the regulatory limits for these facilities. It was found that after settling in the secondary settling tank the phosphate concentration in the wastewater increases, on average, by 110%. For the inhibition of water phosphatizing in the secondary settling tank nitrates were used and an inhibition constant process was installed using 25 $mg \cdot l^{-1}$ nitrate. To prevent pollution of wastewater by phosphates in the secondary settling tank during the regulatory 2 hour settling period, the nitrate concentrations in wastewater have to be above 35 $mg \cdot l^{-1}$.

Keywords: biological wastewater treatment, nutrient removal, phosphating, inhibition, nitrates.

INTRODUCTION

The eutrophication of natural sources of drinking water has become a global problem and so the implementation of highly efficient removal techniques for biogenic elements (nitrogen and phosphorus) is necessary. In countries where supply of potable water relies on surface waters (Central Europe, Northern America and Southern Africa) pollution by nitrogen and phosphorus compounds (eutrophication) is one of the most acute problems for maintaining ecological safety (Lubchenko *et al*., 1996; EPA, 2009). To prevent eutrophication of water bodies and to restore the quality of the aquatic environment it is necessary to minimize emissions of biogenic elements into receivers. Until recently, these elements were mostly discharged from agricultural areas (as surface runoff), however, domestic (municipal) and industrial wastewaters are becoming important sources as well.

Generally, nitrogen and phosphorus compounds are partially removed from municipal wastewater during a conventional biological treatment process performed in activated sludge tanks (aerotanks) or in biofilters. Unfortunately, such processes are not efficient enough, and do not achieve admissible concentrations for wastewater discharged into natural reservoirs. Such efficiency also does not satisfy modern requirements for protecting natural reservoirs against eutrophication.

Application of modern technologies which increase the efficiency of treatment processes at municipal treatment construction – nitrogen and phosphorus compound removal – is considered as a viable option.

The biological methods of nitrogen compound removal are based on microbiological processes with the use of the active sludge, and are considered as the most effective and safe for the environment (Henze *et al*., 1999; Choubert *et al.*, 2005; Yagov, 2008; Gujer, 2010). Transformation of nitrogen compounds during traditional biological treatment process includes the following stages: microbiological assimilation, ammonification, and partial nitrification. During advanced nitrogen removal, additional advanced nitrification and denitrification are introduced. Microbiological nitrification is a chemoautotrophic process occurring in two phases. The ammonium oxidizing bacteria carry out the first phase of nitrification in aerobic conditions, oxidizing ammonium to nitrites (eq. 1):

$$NH_4 + 1.5O_2 \rightarrow NO_2 + 2H^{+} + H_2O \quad (1)$$

In the second phase of nitrification – nitrite bacteria oxidizes nitrites to nitrates in aerobic conditions, as per equation 2:

$$NO_2^- + 0{,}5O_2 \rightarrow NO_3^- \quad (2)$$

To remove nitrites/nitrates from wastewater, a denitrification process is applied (more precisely, dissimilation denitrification). The dissimilation denitrification is a catabolic process of the heterotrophic microbiological reduction of nitrites/nitrates by protons of organic substrates under anaerobic conditions (eq. 3):

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2^{\cdot} \quad (3)$$

The biological phosphorus removal during the traditional biological treatment process is based only on the microbiological assimilation according to the BOD (biochemical oxygen demand): P = 100: 1. The Enhanced Biological Phosphorus

Removal (EBPR) mechanism is based on the following key facts (Kulakovskaja, T. *et al.*, 2014; Phosphorus and nitrogen removal from municipal wastewater: principles and practice. 1991; Henze *et al.*, 2004):

1) phosphate accumulating microorganisms (PAM) are capable of storing excess amounts of phosphorus as polyphosphates;

2) these bacteria are capable of removing simple fermentation substrates produced in the anaerobic zone and assimilating them into storage products within their cells. This process involves the release of phosphorus;

3) in the aerobic zone, energy is produced by the oxidation of storage products and polyphosphate storage in the cell increases.

One term used to descride the anaerobic zone is that it is a 'biological selector' for phosphorus-storing microorganisms. This zone provides a competitive advantage for the phosphorus-storing microorganisms, since they can take up substrates in this zone before non-phosphorus storing bacteria can. Thus, this zone allows the development or selection of a large population of phosphorus-storing organisms in the system which take up significant levels of phosphorus and are removed from the system via the waste sludge. (Phosphorus and nitrogen removal from municipal wastewater: principles and practice. 1991).

At biological phosphorus removal the activated sludge must be exposed to two alternating conditions; an anaerobic (neither oxygen nor nitrate) environment with readily biodegradable substrate and an aerobic environment. In a sequential process this occurs in two phases. In the first phase, the sludge releases phosphate and the concentration of dissolved phosphorus increases (phosphatizing of water), while the soluble COD (chemical oxygen demand) decreases. During the aerobic phase, the sludge takes up phosphate and the concentration of dissolved phosphorus decreases (dephosphatizing of water), normally to a lower value than at the beginning of the cycle (Henze *et al.*, 1999).

Biological phosphorus removal involves design or operational modifications to conventional treatment systems that result in the growth of a biological population that has a much higher cellular phosphorus content. Such systems incorporate an anaerobic operating phase somewhere in the process, and the waste sludge's overall phosphorus content is typically in the range of 3-6 percent. This diverts more phosphorus to the waste solids and yields lower effluent phosphorus concentrations.

Thus, for high-efficiency removal of nitrogen and phosphorus compounds, it is necessary to alternate anaerobic and aerobic treatment of wastewater by activated sludge (EPA, 2009). In the anaerobic step treatment the biological transformation of nitrogen and phosphorus compounds compete for the organic substrate. During biological wastewater treatment a change of aerobic and anaerobic conditions is carried out due to a consecutive passage of the sludge through anaerobic and aerobic zones of the activated sludge tanks (aerotanks) (division of oxygen modes in space) or due to change of anaerobic and aerobic periods of processing in the same reactor of full mixture (division of oxygen modes in time). Reactors in which aerobic conditions (created by pneumatic aeration) and anaerobic conditions (created by stirring) are performed within a single reactor are called the sequencing batch reactors (SBR) (Gujer *et al.*, 2010; Choubert *et al.*, 2005). Many technological schemes have been designed for the efficient removal of nitrogen and phosphorus compounds in the alternation of anaerobic and aerobic treatment zones (Henze, *et al.*, 1999; Gmur, 2003; Henze *et al.*, 2004)

In Ukraine, the majority of wastewater biological treatment plants work under the traditional scheme of 'primary clarifier aerotank secondary settling tank', which is based on the normative documents developed 30 years ago (SNaR 2.04.03-85 "Canalization. External networks and constructions"). These documents are based on the kinetics and efficiency of organic carbon removal (COD, BOD). Nevertheless, the efficiency of nitrogen and phosphorus compound removal during the wastewater biological treatment in such constructions can be improved.

The purpose of this work is efficient management of wastewater from phosphorus compounds in the processing of biological wastewater treatment plants operating under the traditional scheme.

METHODOLOGY OF RESEARCH

Investigations on working wastewater treatment plants in Kharkov city focused on: i) determination of nitrogen compound concentrations (ammonium nitrogen, nitrites and nitrates) and phosphorus compound concentrations (orthophosphate) by standard techniques according to requirements of Ukraine's normative documents; ii) determination of Kjeldahl nitrogen concentrations according to recommendations from literature (Lurie, 1971; Perelik, 1997). Also, data from various stages of biological treatment are presented. *In vitro* investigations were focused on determining nitrate and phosphate concentrations in purified wastewater in sedimentation dynamics (a simulation of processes in the secondary settling tank).

There are two wastewater treatment plants in the Kharkov city with a total capacity of 1.1 million m^3 per day. The sequence of treatment processes at these facilities includes mechanical and biological processes, disinfection and sludge processing (fig. 1). The following study presents results for one of the treatment plants (Kharkov biological wastewater treatment plant, Kharkov WWTP, with capacity of 300 000 m^3) where municipal and industrial wastewaters are delivered.

Construction of the biological reactor at the Kharkov WWTP has been presented in fig. 2.

RESULTS OF RESEARCH

Kharkov city is a big industrial center of Ukraine. The rivers in this region are shallow and contaminated with ammonium nitrogen and orthophosphate received from surface runoff and discharges of untreated wastewater.

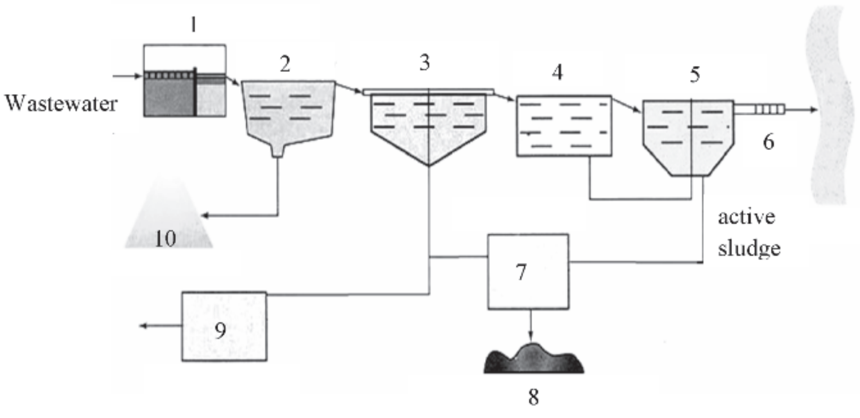

Figure 1. Wastewater Treatment scheme at the Kharkov WWTP: 1 – lattice , 2 – sand trap , 3 – primary clarifier, 4 – aerotank, 5 – secondary settling tank, 6 – disinfection installation, 7 – sludge compactor, 8 – sludge fields, 9 – installation of mechanical dewatering, 10 – sand fields.

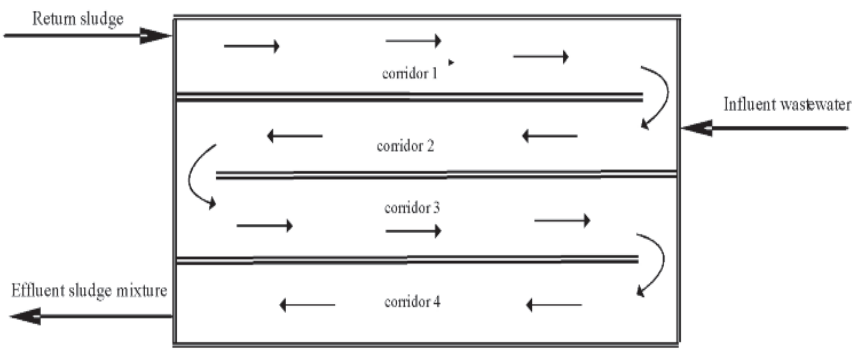

Figure 2. Construction of the plug-flow biological reactor (the aerotank) at the Kharkov WWTP (arrows designate the direction of movement of a liquid)

Indicators of wastewater treatment from biogenic elements in the aeration tank during the dynamics processing are presented in fig. 3, 4. As presented in fig. 3, concentrations of N-NH_4 steadily decline, but particularly rapidly in the first corridor. Nitrite concentrations are constantly minimal. Concentrations of nitrates start to increase in the second corridor of the biological reactor, and reach maximum values at the exit from the biological reactor (the end of fourth corridor). This demonstrates that high activity of the nitrification process, where not only N-NH_4, present in wastewater, is oxidized actively, but also that this form of nitrogen is formed as a result of the mineralization of N_{org}. The residual concentration of N_{org} remains high at the exit from the biological reactor in comparison with EU specifications for wastewater discharged in natural reservoirs. This can be explained by a partial resistance of nitrogen incorporated into organic compounds to the biological oxidation (Henze *et al.*, 1999). Calculation of balance for oxidized and reduced forms of nitrogen in the entrance and exit from the biological reactor testifies, that in the investigated biological reactor, the denitrification process of nitrates and nitrites practically does not occur. As can be seen, the nitrate concentration at the outlet of the aerotank exceeds the allowable 7,9 mg·l^{-1} N-NO_3. However, analysis of the data for the year of work has shown that the average nitrate concentration in the wastewater after treatment in aeration tanks was << 7,9 mg·l^{-1}.

The concentration of P-PO_4 in the incoming wastewater (fig. 4) exceeds the allowable requirements for the Kharkov WWTP (2 mg·l^{-1}).

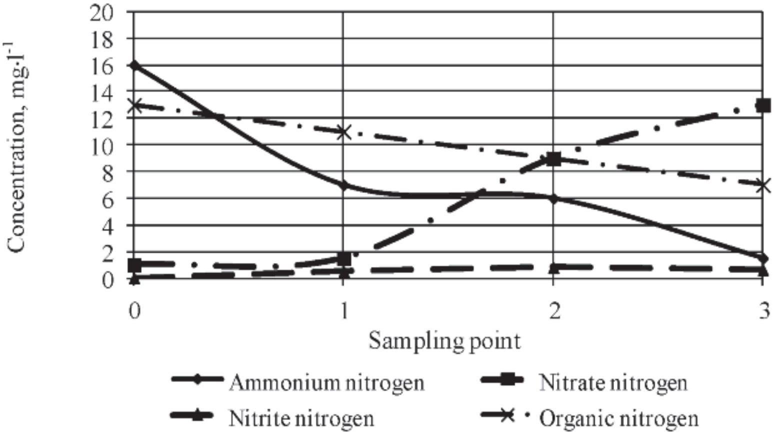

Figure 3. Transformations of different nitrogen compounds during processing treatment in biological reactor at the Kharkov city WWTP (points: 0 entering wastewater, 1 – 2nd corridor, 2 – 3rd corridor, 3 the end of 4th corridor)

As can be seen, the concentration of P_{total} and P-PO_4 in the wastewater, treated in the aerotank, steadily decreases, reaching values at the outlet of the aerotank of 2,0 and 1,9 mg·l^{-1}, respectively.

The results of the survey of the system 'aerotank- secondary settling tank' show that the phosphate concentration in wastewater after settling steadily increases (fig. 5).

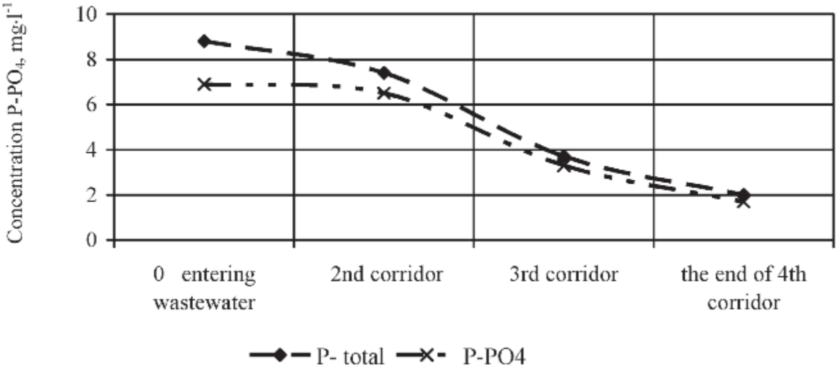

Figure 4. Transformations of phosphorus compounds during processing treatment in biological reactor at the Kharkov city WWTP (points: 0 entering wastewater, 1 – 2nd corridor, 2 – 3rd corridor, 3 the end of 4th corridor)

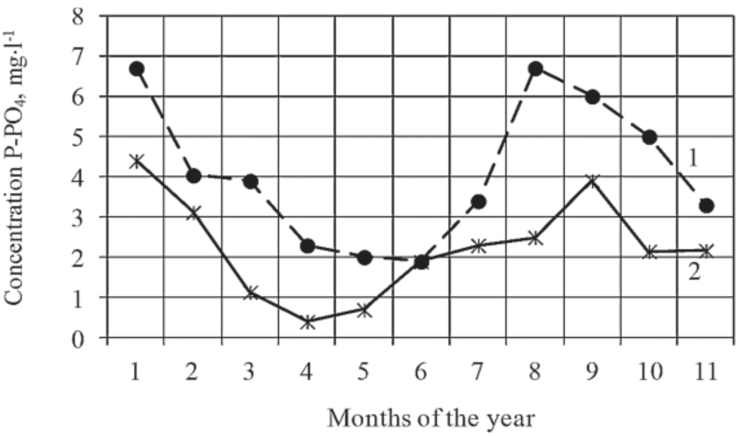

Figure 5. Monthly average concentrations of P-PO4 in wastewater at treatment stages: 1 – wastewater after aerotank, 2 – wastewater after secondary settling tank

The presence of nitrates in the treated wastewater is a positive development as evidence of the passage of a full biological treatment with nitrification. It is known that nitrates inhibit phosphatizing of water, but the quantitative characteristics of the process according to different authors vary greatly. In addition, the nitrate concentration in the effluent discharged into a natural water source has a limited MPC (maximum permissible concentration) of 30-45 mg·l^{-1}. As shown the results of laboratory research into the process of settling reveal that the concentration of effluent phosphate increased steady (table 1).

Table 1

The effect of the duration of the sedimentation of sludge liquid on the concentration of phosphates and nitrates in wastewater

Settling time	Phosphates, $mg \cdot l^{-1}$	Nitrates, $mg \cdot l^{-1}$
0	11,56	47,7
20	11,76	
30	15,84	
60	16,0	
120	16,2	39,2
180	16,5	
210	18,0	30,9

In experiments with settling of wastewater with different concentrations of nitrates, obtained data revealed a relationship shown in fig. 6. From the data of fig. 6 it is clear that with increasing nitrate concentrations from 0 to about 45 $mg \cdot l^{-1}$ the phosphatizing speed falls in a linear relationship.

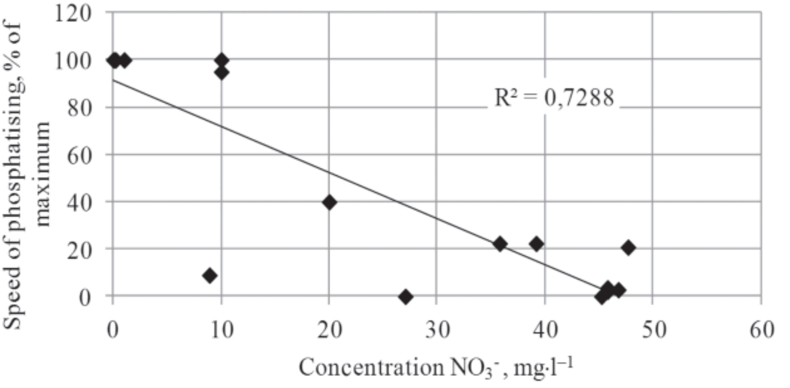

Figure 6. Influence of nitrate concentrations in treated wastewater on their phosphatizing during settling

DISCUSSION

Required treatment efficiency is based on standards for treated effluent discharged into water bodies. Different values of admissible nitrogen and phosphorus concentrations are presented in table 1. In EU countries, only the total concentration of nitrogen and total concentration of phosphorus in wastewater are standardized, and in eutrophication sensitive areas, they should not exceed 15 $mg \cdot l^{-1}$ and 2 $mg \cdot l^{-1}$

(respectively) for wastewater from settlements with up to 100 thousand person equivalents (PE), and 10 mg·l^{-1} and 1 mg·l^{-1} (respectively) for wastewater from settlements with over 100 thousand PE. In Ukraine, only soluble mineral nitrogen and phosphorus forms are under scrutiny. For fish farming reservoirs the admissible concentration of mineral soluble nitrogen is 9,55 mg·l^{-1} and standardization of phosphorus compounds concentrations is absent. For reservoirs used for drinking supply the admissible concentration of mineral soluble nitrogen is 13,16 mg·l^{-1} and the admissible concentration of mineral soluble phosphorus is 1,14 mg·l^{-1}. Concentrations of organic nitrogen and organic phosphorus are not supervised, and the absence of this control parameter extremely complicates the rational organization of wastewater treatment process, and also diminishes the efficiency of the eutrophication protection measures.

Changing N-NH_4, N-NO_2, N-NO_3 and N_{org} concentrations in wastewater in the aeration tank during processing proves high activity of the nitrification process, where not only N-NH_4, present in wastewater, is oxidized actively, but also that this form of nitrogen is formed as a result of the mineralization of N_{org}. The concentration of N_{total} = N-NH_4+ N-NO_2+ N-NO_3+N_{org} in the treatment wastewater at the exit from the biological reactor exceeds EU specifications for wastewater discharged into natural reservoirs. Calculations of the balance of oxidized and reduced forms of nitrogen in the entrance and exit from the biological reactor testifies that in the investigated biological reactor the denitrification process of nitrates and nitrites practically does not occur. Concentrations of N-NO_3 in the treated wastewater sometimes exceeds admissible concentration for Kharkov WWTP (7,9 mg·l^{-1} or 35 mg·l^{-1} nitrates). Because concentrations of BOD_5 in wastewater exceeds 110 mg·l^{-1} at the entrance to the biological reactor, denitrification of more than 28 mg·l^{-1} N-NO_3 is possible through partial recycling of treated wastewater at the entrance to the biological reactor.

The P-PO_4 concentration in the incoming wastewater is up to 70% of the P_{total} content. The concentration of P-PO_4 in the incoming wastewater exceeds the admissible concentration for Kharkov WWTP (2 mg·l^{-1}). The share of P-PO_4 in the treated wastewater increases, reaching an average of 85% P_{total}. This indicates that the removal of phosphorus compounds extends deeply, and its residual compounds are inorganic biologically non-degradable substances. Aerotank residual concentrations of P-PO_4 in most cases (fig. 5) exceed allowable standards for Kharkov WWTP (0,7 mg·l^{-1}). After treatment of wastewater in the secondary settling tank (fig. 4) the concentration of P-PO_4 increases from 0 to 233% (on average by 110%). In laboratory experiments that simulate the processes in the secondary sedimentation tanks, the concentration of phosphates in wastewater after the normative duration of settling (2 hours) increased by 42% with a parallel decrease in the nitrate concentration. This corresponds with data in scientific literature about the migration of phosphates in system activated sludge - wastewater under anaerobic conditions (Henze *et al.*, 2004; Phosphorus and nitrogen removal from municipal wastewater: principles and practice. 1991; EPA, 2009; Yurchenko, V. *et al.*, 2015).

Table 2

Admissible concentrations of nitrogen and phosphorus in wastewater

Country	Sources of wastewater	Controllable parameter	Admissible concentration ($mg \cdot l^{-1}$)
European Union countries	Wastewater from settlements up to 100 thousand PE	Total nitrogen	15
		Total phosphorus	2
	Wastewater from settlements above 100 thousand PE	Total nitrogen	10
		Total phosphorus	1
Ukraine	Reservoirs at fish-farms	$N\text{-}NH_4$	0,5
		$N\text{-}NO_2$	0,02
		$N\text{-}NO_3$	9,03
		$P\text{-}PO_4$	absent
	Reservoirs of drinking water	$N\text{-}NH_4$	2,0
		$N\text{-}NO_2$	1,0
		$N\text{-}NO_3$	10,16
		$P\text{-}PO_4$	1,14

From the obtained dependence (fig. 5), the inhibition constant of phosphatizing of treated wastewater in a secondary settling tank by nitrates can be installed – the nitrate concentration at which the inhibition of the phosphatizing rate occurs is 50%. This constant has a value of 22 $mg \cdot l^{-1}$ nitrates or 5,0 $mg \cdot l^{-1}$ $N\text{-}NO_3$. During settling the nitrate concentration decreases at a rate 4.8 $mg \cdot (l \cdot h)^{-1}$, i.e. after the normative 2 hours settling – to 9,6 $mg \cdot l^{-1}$ or 2,2 $mg \cdot l^{-1}$ $N\text{-}NO_3$. If the regulatory allowable concentration of nitrate in the effluent is not more than 35 $mg \cdot l^{-1}$ or 7,9 $mg \cdot l^{-1}$ $N\text{-}NO_3$ (the admissible concentration for Kharkov WWTP) after 2 hours settling their residual concentration is not more than 26 $mg \cdot l^{-1}$ or 5,7 $mg \cdot l^{-1}$ $N\text{-}NO_3$. Based on this concentration phosphatising in a secondary settling tank has to be suppressed by at least 50%. Considering the reduction of the nitrate concentration in the secondary settling tank after 2 hours of settling, settling tank water will have a concentration of $N\text{-}NO_3 = 7{,}9 + 2{,}2 = 10{,}1$ $N\text{-}NO_3$ $mg \cdot l^{-1}$ or 44,7 $mg \cdot l^{-1}$ nitrate. In the secondary settling tank phosphatising will be inhibited by almost 100%. A residual concentration of nitrate will not exceed regulatory requirements.

CONCLUSIONS

The current study based on the Kharkov WWTP allowed us to draw the following conclusions:

- The total load of ammonium nitrogen and organic nitrogen on the biological reactors is extremely high due to the concentration of ammonium nitrogen exceeding allowable levels;
- Treatment processes in the biological reactors with active sludge include deep nitrification, while the denitrification process does not occur at all;
- The most effective way to increase efficiency of the nitrogen and phosphorus compounds removal is to the increase time of the aerobic treatment to allow advanced oxidation of organic compounds and to improve the nitrification process (decrease of residual ammonium nitrogen concentration);
- The concentration of $P\text{-}PO_4$ in the incoming wastewater exceeds the allowable requirements for Kharkov WWTP.
- To prevent pollution of treated wastewater by phosphates in the secondary settling tank, the retention time of settling must consider the nitrate concentrations in wastewater. Phosphatizing of the water is minimal at the nitrate concentration above 35 $mg \cdot l^{-1}$ and retention time of settling 2 hours.
- Modernization of the investigated facility shall also point out the necessity of improving of standardization for nitrogen and phosphorus compound concentrations in Ukrainian wastewaters.

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