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THE INFLUENCE OF NITRATE ON THE PHOSPHATE REMOVAL FROM WASTEWATER IN ACTIVATED SLUDGE TREATMENT PROCESS

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The aim of the research was to determine the degree of influence of wastewater nitrate concentration on the process of removal of phosphorus compounds by sequential water treatment in anoxic and aerobic conditions in an activated sludge system. Model wastewater solutions were used for research with following parameter: biochemical oxygen demand for 20 days $-200 \text{ mgO}_2/\text{l}$; phosphate concentrations -11.87-12.38 mg/l; nitrate concentrations -21.0; 36.0 and 48.0 mg/l. Activated sludge was added to them with content in solutions 2.2 mgO₂/l to provide biological processes. For simulation of the biological process of dephosphotation in wastewater with usage of activated sludge in sequentially formed anoxic and aerobic conditions, a model sequential reactor - SBR reactor - was used. As the results show, with the increase in the concentration of nitrates at the inlet from 21.0 to 48.0 mg/l, the phosphate concentration in the treated solutions at the outlet from the bioreactor increases by 7.3%. Thus, from the work presented here, it can be concluded that for successful and effective implementation of the dephosphotation process the elimination of the nitrate present in wastewater is required. It is reasonable to separate processes of denitrification and dephosphotation in separate structures with the provision of minimal nitrate influence on the phosphorus removal from wastewater.

Key words: wastewater, dephosphotation, activated sludge.

Increasing pollution of natural waterbodies by compounds of nutrients that come from insufficiently treated wastewater as a communal, as well as industrial origin, leads to an increase of eutrophication processes in water sources. The results are: the rapid development of aquatic plants and algae, water pollution, reduction of oxygen concentration in water, deterioration of the waterbodies state, strengthening of saprogenic processes, reduction of the hydrobionts species diversity, etc.

Biological and physico-chemical purification technologies are used for wastewater treatment from nitrogen and phosphorus compounds [1, 2]. Recently, biological methods based on processes of denitrification for the removal of nitrate from wastewater and dephosphotation for the removal of phosphorus compounds are becoming more widespread [3–8]. In such methods, activated sludge is used and certain conditions for wastewater treatment are created. Thus, for dephosphotation it is necessary to create sequentially anaerobic and aerobic conditions [9, 10]. Then, in anaerobic conditions, activated sludge is stressed, and, consequently, it accumulates granules of polyphosphate in the bacterial cells, decomposition of which generate energy for bacteria [11, 12]. In aerobic conditions, bacteria accumulate phosphate in excess amounts, which is removed from water. They receive energy as a result of the decomposition of polyhydroxyalcanoates or polyhydroxybutyrate, which are synthesized by the cells under anaerobic conditions [12]. For the growth and development of bacteria in the processes of dephosphotation of wastewater, they need the presence of carbon sources easily digested by cells, for example, volatile fatty acids: acetic, propionic, etc. [12, 13].

According to recent studies of the dephosphotation processes in wastewaters, the degree of phosphorus compounds removal affected by the nitrate concentration, because in anaerobic conditions denitrification is possible in parallel with dephosphotation [14–17]. Bacteria that remove nitrate from water — denitrifiers, as well as bacteria that remove phosphate, require carbonaceous compounds that are easily digestible by them in anaerobic conditions [18, 19]. Thus, the question arises whether the process of denitrification will inhibit the activity of bacteria that remove phosphorus from the water and, if so, at what degree [20].

The purpose of research was to determine the degree of influence of nitrate concentration in wastewater on the process of removal of phosphorus compounds with the use of sequential water treatment in anoxic and aerobic conditions in an activated sludge system.

Material and Methods

An activated sludge from the Bortnychi aeration station in Kyiv city was used to conduct the research. Mixed liquor suspended solids (MLSS) was 5.5 mg/l and activated sludge contains microorganism's groups which are inherent for correct operation of aeration tanks with sufficient aeration, concentration of organic compounds and biogenic substances. Model wastewater solutions were used for research. BODfull – 200 mgO₂/l was provided with the addition of sucrose. Activated sludge was added to them with MLSS 2.2 mgO₂/l in solutions to provide flow of biological processes. Concentration of phosphate was 11.87–12.38 mg/l; concentration of nitrate at values 21.0; 36.0 and 48.0 mg/l was provided by addition of KNO₃ solution.

For simulation of the biological process of dephosphotation in wastewater with usage of activated sludge in sequentially formed anoxic and aerobic conditions, a model SBR (Sequencing Batch Reactor) with a working water volume of 300 cm^3 was used. Initially, anoxic conditions were created in the bioreactor, which contained wastewater with activated sludge for 2 h with constant mixing by the pump. After that, the pump was switched off and aeration of an activated sludge mixture was carried out for 4 h with the aid of a microaerator. The concentration of dissolved oxygen in the aeration zone was 2.0 mgO₂/l, the aeration intensity was 8 cm³/ (cm_2 ·min). Adaptation time of activated sludge to experimental conditions was 1 day.

Wastewater sampling was carried out at the beginning of the treatment, after anoxic and after aerobic processes. 3 points were obtained for each model solution of the biological treatment process in a bioreactor, with the definition of mean values of analysis result. Dependency diagrams were built from the mean values.

Chemical analyzes for determination of the nitrate and phosphate concentrations in wastewater samples were carried out using standard techniques: nitrate — colorimetric method with salicylic acid; phosphate colorimetric method with ammonium molybdate. Accuracy of analysis for nitrate concentration — ± 0.5 mg/l, phosphate — ± 0.01 mg/l.

All experiments were performed in triplicate. Statistical data analysis were was conducted using Microsoft Excel software. Difference between two average values was considered significant at P < 0.05.

The removal rate of phosphate from water was determined by the formula:

$$E (P_2O_5) = [C (P_2O_5)in - C (P_2O_5)_i]/C (P_2O_5)_{in} \times 100, \%;$$

with C (P_2O_5) in — initial concentration of phosphate in the model solution (at the inlet to the SBR-reactor); C (P_2O_5) i — concentration of phosphate in the model solution after treatment by *i* hours (2 h and 6 h).

The removal rate of nitrate from water was determined by the formula:

$$E (NO_3^{-}) = [C (NONO_3^{-})_{in} - C (NONO_3^{-})_{i}] / /C (NONO_3^{-})_{in} \times 100, \%;$$

where C (NO₃⁻)in — initial concentration of nitrate in the model solution (at the inlet to the SBR-reactor); C (NONO₃⁻)i — concentration of nitrate in the model solution after treatment by *i* hours (2 h and 6 h).

Results and Discussion

The results of model solutions treatment in sequential anoxic and aerobic conditions of a bioreactor in relation to variation of phosphate concentration for 6 hours are presented in Fig. 1.

As can be seen from the graphs obtained, with an increase in the concentration of nitrate in the model solution from 21.0 to 48.0 mg/l, there is an effect on the final content of phosphate in the solution after treatment with activated sludge. The greatest decrease in the concentration of phosphates at the end of aerobic conditions was obtained at a nitrate concentration of 21.0 mg /l (Fig. 1, graph 1). At higher concentrations of nitrates lower phosphate removal from solutions was obtained (Fig. 1, graphs 2 and 3).



Fig. 1. The variation of phosphate concentration C (P_2O_5) in activated sludge process with hydraulic residence time t and initial concentration of nitrate, mg/l: 1 - 21.0; 2 - 36.0; 3 - 48.0;

*Compared to a control model solutions without addition of activated sludge P < 0.05

Graphic dependencies were build, as show on Fig. 2, in order to evaluate the degree of phosphate removal rate with hydraulic residence time of solutions in the SBR-reactor under the sequential anoxic (2 hours) and aerobic conditions (6 hours). The graphs clearly show, that the removal rate of phosphate by activated sludge from model solutions decreases with increasing initial concentration of nitrate in solutions from 21.0 to 48.0 mg/l. The largest removal rate of phosphates in sequential anoxic-aerobic conditions is observed at the lowest initial concentrations of nitrates in the solution -21.0 mg/l. With such concentration of nitrates, the removal rate of phosphate in the presence of nitrate in the solution reaches 5.5%. Further increase of the initial nitrate concentration up to 48.0 mg/l leads to a significant decrease in the removal rate of phosphate from solutions up to 2%. This testifies to the competition between microbial groups of activated sludge (denitrifiers and phosphate accumulating bacteria) and less activity of phosphate accumulating microorganisms in the presence of nitrate concentrations more than 21.0 mg/l insolutions, which leads to inhibition of wastewater dephosphotation [13] including domestic wastewater, it is necessary to concentrate phosphorus in order to make recovery and reuse feasible. This review discusses enhanced biological phosphorus removal (EBPR).

In addition, a variation in the concentration of nitrates in the model solutions was

determined when they were treated in an SBR-reactor with an activated sludge under different oxygen conditions — anoxic at the beginning of treatment (2 hours) and subsequent aerobic (4 hours). The results are presented in Fig. 3 and 4 at different initial concentrations of nitrate — 21.0 and 36.0 mg/l, respectively.

As shown in Fig. 3 and 4, graphs indicate variation of nitrate concentrations in solutions during the process of their treatment in the SBR-reactor. Decrease of nitrate concentration in solutions at the anoxic conditions is explained by the process of denitrification, which takes place with the participation of activated sludge and the presence of carbon source in solution. Further, some increase in the nitrate concentration indicates the processes of nitrification occurring in an activated sludge in aerobic conditions with the conversion of ammonium nitrogen compounds into nitrates

In order to evaluate the removal rate of nitrate from solutions by activated sludge process, the results are presented in the form of graphs given in Fig. 5. At initial concentrations of nitrates 21.0 and 36.0 mg/l, their removal rates are 9.5% and 3.5% correspondingly in model solutions at the end of anoxic treatment. In an aerobic activated sludge process, the removal rate of nitrates from wastewater decreases due to the additional nitrate input as a result of nitration process of ammonium compounds, as noted



Fig. 2. Phosphate removal rate E (P_2O_5) in activated sludge process with hydraulic residence time t and initial concentrations of nitrate, mg/l: 1 - 21.0; 2 - 36.0; 3 - 48.0

*Compared to a control model solutions without addition of activated sludge P < 0.05



Fig. 3. The variation of nitrate concentration C (NO⁻₃) in activated sludge process with hydraulic residence time t and initial concentrations of nitrate 21.0 mg/l *Compared to a control model solutions without addition of activated sludge P < 0.05



Fig. 4. The variation of nitrate concentration C (NO₃) in activated sludge process with hydraulic residence time τ and initial concentrations of nitrate 36.0 mg/l *Compared to a control model solutions without addition of activated sludge P < 0.05</p>



Fig. 5. Nitrate removal rate E (NO $_3$) in activated sludge process with hydraulic residence time t and initial concentrations of nitrate, mg/l: 1 - 21.0; 2 - 36.0; 3 - 48.0

*Compared to a control model solutions without addition of activated sludge P < 0.05



Fig. 6. Dependence of phosphate concentration C (P₂O₅) at the end of aerobic treatment on initial nitrate concentration C (NO⁻₃) *Compared to a control model solutions without addition of activated sludge P < 0.05

above (as a result of the processes associated with the bacterial activity). Therefore, the removal rate of nitrates in aerobic conditions decreases, as shown in graphs 1 and 2 (Fig. 5).

The generalized correlation between the initial nitrate concentration in solutions (at the inlet of the SBR reactor) and the concentration of phosphates in treated sequential anoxic and aerobic conditions (at the outlet of the SBR reactor) is presented in Fig. 6. As the results show, with the increase in the concentration of nitrates at the inlet from 21.0 to 48.0 mg/l, the phosphate concentration in the treated solutions at the outlet from the bioreactor increases by 7.3%. This indicates the effect of nitrates on the process of wastewater treatment from phosphates, which confirms the competitive relationship between denitrifiers and phosphorus-accumulating bacteria of activated sludge for the source of carbonaceous compounds and the advantage of the denitrifiers [16].

Thus, from the work presented here, it can be concluded that for successful and effective implementation of the dephosphotation process the elimination of the nitrate present in wastewater is required. During the process

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ВПЛИВ НІТРАТІВ НА ВИДАЛЕННЯ ФОСФАТІВ ЗІ СТІЧНИХ ВОД ПРИ ОЧИЩЕННІ З АКТИВНИМ МУЛОМ

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Метою роботи було встановити ступінь впливу концентрації нітратів у стічній воді на процес видалення сполук фосфору в разі застосування послідовного оброблення води в аноксидних і аеробних умовах у системі з активним мулом. Було використано модельні розчини стічної води з показником біохімічна потреба у кисні за 20 днів — 200 мгО₂/дм³; концентраціями фосфатів 11,87-12,38 мг/дм³; нітратів — 21,0; 36,0 і 48,0 мг/дм³. Для забезпечення процесів біологічного очищення застосовували активний мул із вмістом у розчинах — 2,2 г/дм³. З метою моделювання біологічного процесу дефосфотації стічних вод в аноксидно-аеробних умовах було використано модельний реактор послідовно-змінної дії — SBR-реактор. Як показують одержані результати, за зростання концентрації нітратів на вході з 21,0 до 48,0 мг/дм³ концентрація фосфатів у оброблених розчинах на виході з біореактора зростає на 7,3%. Таким чином, з проведеної роботи можна зробити висновок про те, що для успішного й ефективного здійснення процесу дефосфотації та усунення впливу нітратів доцільно розділяти процеси денітрифікації та дефосфотації в окремих спорудах із забезпеченням мінімального впливу нітратів на видалення з води сполук фосфору.

Ключові слова: стічні води, дефосфотація, активний мул.

ВЛИЯНИЕ НИТРАТОВ НА УДАЛЕНИЕ ФОСФАТОВ ИЗ СТОЧНЫХ ВОД ПРИ ОЧИСТКЕ С АКТИВНЫМ ИЛОМ

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Целью работы было установить степень влияния концентрации нитратов в сточных водах на процесс удаления соединений фосфора при использовании последовательной обработки воды в аноксидных и аэробных условиях в системе с активным илом. Были использованы модельные растворы с показателем — биохимическая потребность стока в кислороде за 20 дней — 200 мгО₂/дм³; концентрациями фосфатов 11,87-12,38 мг/дм³; нитратов — 21,0; 36,0 і 48,0 мг/дм³. Для обеспечения процессов биологической очистки применяли активный ил с содержанием в растворах — 2,2 г/дм³. Для моделирования биологического процесса дефосфотации сточных вод в аноксидно-аэробных условиях был использован реактор последовательно-переменного действия — SBR-реактор. Как показывают полученные результаты, при возрастании концентрации нитратов на входе с 21,0 до 48,0 мг/дм³ концентрация фосфатов в обработанных растворах на выходе из биореактора возрастает на 7,3%. Таким образом, на основании выполненной работы можно сделать вывод о том, что для успешного и эффективного осуществления процесса дефосфотации и устранения влияния нитратов целесообразно разделять процессы денитрификации и дефосфотации в отдельных сооружениях с обеспечением минимального воздействия нитратов на удаление из воды соединений фосфора.

Ключевые слова: сточные воды, дефосфотация, активный ил.

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