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PHOSPHORUS RELEASE FROM EXCESS ACTIVATED SLUDGE TO SLUDGE LIQUIDE UNDER AEROBIC AND ANAEROBIC SLUDGE STABILIZATION

A limited number of known reserves of phosphorus and avoiding eutrophication of water bodies are the driving forces to search and study ways to extract phosphorus from wastewater and sludge treatment plants.

It is shown that the phosphorus of excess activated sludge can release into sludge water during sludge treatment. This water is returned to the head of wastewater treatment plant, thereby increasing the phosphorus load to the biological treatment system. The aim of this study was to establish patterns of phosphorus transition in sludge water under different condition of activated sludge stabilization. The object of the study was the suspension of thickened activated sludge from Minsk treatment plant (MTP). The modeling process treatment of excess active sludge was carried out in laboratory settings of volume 2.5–6.0 dm³.

There were established the dependences of phosphorus content and pH value during prolonged thickening of aerobic and anaerobic stabilization. It is shown that the most insensitive phosphorus release from excess active sludge to supernatant takes place under anaerobic treatment during first three days. Under these conditions the concentration of phosphorus in sludge water increased up to 300 mg P/dm³. During prolonged anaerobic treatment the release of phosphorus depends on hydrodynamic conditions. Up to 80% of the total phosphorus content in the excess activated sludge is released without stirring. Under aerobic conditions, the yield of phosphorus in the sludge water is determined by the air flow rate and processing time and can be up to 387 mg P/dm³.

Key words: excess active sludge, phosphates, wastewater treatment, sludge treatment.

Introduction. The limited and exhaustible of explored reserves of phosphorus-containing raw materials [1], irreplaceability of phosphorus for food production stipulates the necessity of searching for ways of extraction from wastes and wastewater.

The features of biogeochemical cycle of phosphorus are: lack of stable gaseous compounds, which leads to its concentration in the lithosphere and hydrosphere; biological significance, since often it is the phosphorus that limits the biomass growth [2].

Significant impact on the natural phosphorus cycle has increased the use of its resources for the production of fertilizers, detergents, etc. [3]. The result of human activity is technogenic phosphorus cycling from extraction of phosphorus-containing raw material extraction to consumption of the products, mainly food and detergents. A significant role plays the migration of phosphorus with wastewater as well as excessive accumulation in water bodies. Annually about 20 Mt of phosphorus is produced and about 50% of this amount falls into water bodies [4].

At wastewater treatment plants phosphorus is removed from the waste water with primary sludge and excess activated sludge (EAS) (Fig. 1).

The intensification of the removal of phosphates is provided by biological dephosphatation based on the cultivation of phosphorus accumulating organisms (PAOs) being capable to accumulate phosphorus in amount exceeding their own needs [6].

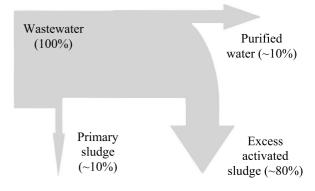


Fig. 1. Removal of phosphorus at wastewater treatment plants (based on the data source [5])

Biological phosphorus intake is associated with its inclusion in the composition of cells, mainly nucleic acids and structural replacement substances and energy metabolism. For the course of "greedy" consumption and accumulation of phosphorus by PAO cells in the condition of aeration it is necessary to subject them to "prestressing" under anaerobic conditions. Phosphates are released into the environment by the cells in the absence of dissolved oxygen and the presence of easily oxidizable organic, herewith using the energy for accumulating simple organic substances such as polyhydroxyalkanoates (most common poly-β-hydroxybutyrate (PHB)). Under aerobic conditions, the PHB accumulated is used by the cells as a power source, which is

Ecology 201

accompanied by the accumulation of phosphate from sewage [6–9].

The peculiarity of biological dephosphatation is the reversibility of the process of accumulation of phosphates. While processing precipitation, phosphorus can be released into the liquid phase of the sludge suspension. The destruction of polyphosphates and release of phosphorus in the form of phosphate is observed at [7, 8, 11–14]:

- long stay of the sludge in secondary sedimentation tanks;
 - gravitational thickening of EAS;
 - stabilization of sludge;
 - mechanical sludge dewatering;
- thickening of sewage sludge on the sludge lagoons.

These processes, except for the first, followed by the formation of sludge water that returns to the receiving chamber of treatment plants (return flow).

There are several theories to explain the phosphorus release during the processing of EAS: desorption from the surface of the activated sludge flakes [6]; intracellular degradation of phosphorus compounds, accompanied by return of accumulated phosphorus into water [7–9]; death of the aerobic bacteria and cellular autolysis induced by changes in ambient conditions (lack of dissolved oxygen, the hydrodynamic conditions change, etc.) [10, 11].

With the return flow one can get into the purification system up to 30% of the phosphorus contained in the wastewater inflowing for the purification [12, 14]. This leads to the fact that the return of sludge water into the receiving chamber of the treatment facilities reduces cleaning efficiency of wastewater from phosphorus in general [7, 8, 12–14].

To return the phosphorus accumulated by activated sludge into the economy, it is necessary to

provide the use of the resulting sewage sludge. However, more than 50% of the resulting amount of precipitation has a number of limitations for the usage in agriculture, caused by a high content of heavy metals, persistent organic pollutants, drugs, etc. [15]. In this case, one of the variants of using phosphorus entering the treatment plant, is its extraction from a sludge water. Thus it is necessary to create conditions of maximum transition of phosphorus into a liquid phase of sludge slurry for its subsequent retrieval in a form available for use. However, the available data do not allow to predict the content of phosphates in return flows, depending on the conditions of precipitation treatment.

The goal of the work was to establish regularities of transition of phosphate into the sludge water during the aerobic and anaerobic treatment of excess activated sludge.

Materials and methods of investigations. The object of the study was sludge suspension of Minsk treatment plant first stage (MTP-1), selected after sludge thickener with moisture of 98.2%, ash content of 24.4% and the total content of phosphorus of 571 mg P/dm³. Total phosphorus content was determined in accordance with [17], humidity and ash content before and after stabilization were determined gravimetrically.

The effect of the conditions of excess activated sludge treatment on phosphorus redistribution between phases of sludge suspension was determined for the aerobic and anaerobic stabilization.

The processes of aerobic and anaerobic treatment of activated sludge were simulated in the bioreactors of batch operation with volume of 2.5; 3.0 and 6.0 dm³ (Fig. 2) operating in psychophilic $(20 \pm 1,5)^{\circ}$ C mode. The duration of treatment in all cases was 23 days.

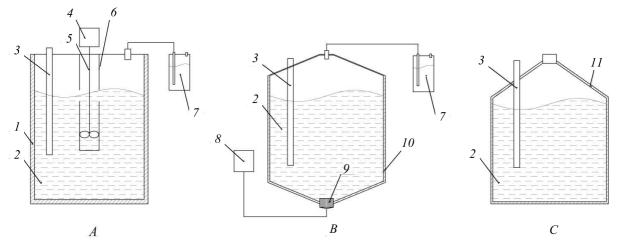


Fig. 2. Experimental facilities:

- A anaerobic reactor with stirring; B aerobic reactor; C anaerobic reactor; l metal container of 2.5 dm³; 2 sludge suspension; 3 sampling tube;
- 4 electric motor; 5 mixer; 6 guide tube; 7 hydraulic lock; 8 air blower; 9 perforated plate; 10 Plexiglas reactor of 3 dm³; 11 plastic reactor of 6 dm²

Anaerobic stabilization was carried out in two modes: with and without agitation. Excess activated sludge was not stirred in the reactor (Fig. 2, B). The sealed bio reactor (Fig. 2, A) is equipped with a paddle stirrer with electrical drive and hydraulic lock (absorber with 0.01 M solution of alkali).

Aerobic stabilization was carried out in the bioreactor (Fig. 2, B) while sludge suspension is aerated with air flow of 54 and 40 m³/m³ · h. Gas withdrawal was accomplished through the absorber with 0.01 M alkaline solution.

Control of phosphorus transition into the liquid phase of the sludge slurry was performed by measuring the phosphate content and pH of the sludge water. Daily samples of sludge suspension were taken through the pipe 3, and centrifuged at 8,000 min⁻¹ for 10 minutes followed by decantation of the liquid phase. On the first day for the anaerobic conditions without stirring, the analysis of sludge suspension samples was carried out every hour for the first eight hours. Phosphate concentration was determined by photocolorimetry method in accordance with STB ISO 6878-2005 [16], while the concentration values were counted on phosphorus. The pH value was measured by the potentiometric method on pH-meter I – 160.1 MT with combined electrode ESKL-08M.1.

Results and discussion. The anaerobic treatment of the compacted activated sludge suspension of MTP-1 decreases the volume of EAS and increases its ash to 31.3 and 30.8%, respectively, while stirring and without it, which is accompanied by an increase in the concentration of phosphate in the sludge water (Fig. 3). For the first three days regardless of hydrodynamic conditions, the release

of phosphorus into the liquid phase of the sludge suspension is the most intensive. Herewith the content of phosphate in the sludge water is increased to three times compared with the original from 90 to 300 mg P/dm³, which agrees with previously obtained data [7].

As it is known, the indispensable condition of intensive anaerobic conversion process is an adequate mass transfer inside the reactor, which is necessary for the efficient transport of substrates to microorganisms, the elimination of local accumulations of intermediates, maintain of uniform conditions throughout the reactor volume (temperature, dissolved oxygen etc.), which promotes cell development [18, 19].

The comparison of the graphs of dependencies in changes of phosphate concentration in time (Fig. 3) allow us to make a conclusion that the process of release of phosphorus in the liquid phase under anaerobic stabilization is also influenced by the hydrodynamic conditions of the process. In the absence of mixing the phosphate concentration in water sludge increases on the 12th day to value of 450 mg P/dm³; then the concentration remains practically unchanged. Accordingly, the share of released phosphorus is 79% of the gross amount of phosphorus. The dependence of phosphorus release in anaerobic conditions without stirring has several inflection points corresponding to 3 and 12 days, which shows the change in flow rate of the process and the reasons that lead to the transition. For the first three days the increasing of phosphate concentration is likely to be connected mainly with using of the energy reserves of polyphosphates by cells, and for 3–12 days with the cellular autolysis.

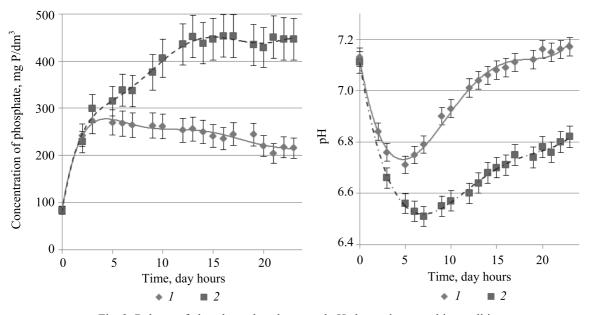


Fig. 3. Release of phosphate phosphorus and pH change in anaerobic conditions: I – anaerobic reactor with stirring; 2 – anaerobic reactor without stirring

Ecology 203

But in the mode of mixing the phosphate concentration increases only in the first three days, then the concentration declines gradually from 273 to 210 mg P/dm³, due to adaptation and development of anaerobic microorganisms.

The process of phosphorus release was examined in detail under anaerobic conditions during the first day (Fig. 4).

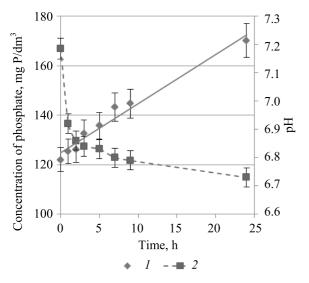


Fig. 4. Changing the concentration of phosphate and pH in the sludge water during prolonged thickening:

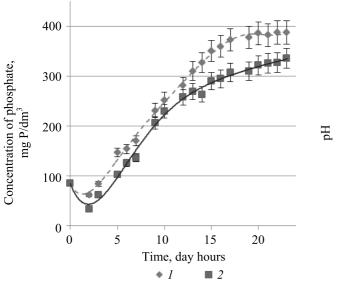
1 – phosphate concentration; 2 – pH

During the first day of the extended sealing under anaerobic conditions phosphate concentration increases linearly. At the same time one can observe a decrease in pH. Prolonged exposure to anaerobic conditions is characterized by reducing the pH. Thus, under stirring, the pH is lowered to 6.7 for five days, in the absence of stirring it is lowered to 6.5 for seven days. The further course of anaerobic stabilization is accompanied by an increase in pH. Acidation occurs primarily due to the formation of volatile fatty acids (VFA), hydrogen sulphide as well as CO₂ emissions.

Alkalization of the medium occurs through the consumption of VFA and deaminization of nitrogen-containing compounds [18], as well as the production of bicarbonate [19].

Fig. 5 presents the results of the research of the air consumption influence on transition of phosphates into liquid phase under aerobic stabilization. Smaller speed of transition of phosphorus into the liquid phase is typical for aerobic stabilization in comparison with anaerobic conditions. By increasing the air consumption, more intense transition of phosphorus in sludge water can be observed. The linear dependence of increase in concentration over time can be observed in the dependence of the change of phosphate concentration in the period from 2 to 17 days.

The aerated conditions reduce phosphate concentration in the samples of sludge water in the first two days in both cases, it is reduced from the initial 84 mg P/dm³ to 33 and 62 mg P/dm³, respectively, for air consumption of 40 and 54 m³/m³ · h. This can be explained by the fact that aeration leads to an intensification of life activity of aerobic bacteria, and hence the phosphorus intake [19].



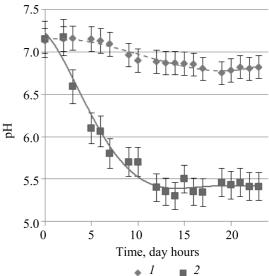


Fig. 5. Release phosphate phosphorus and changing the pH under aerobic conditions: $I - \text{air consumption } 54 \text{ m}^3/\text{m}^3 \cdot \text{h}; 2 - \text{air consumption } 40 \text{ m}^3/\text{m}^3 \cdot \text{h}$

After two days of aeration, there is a gradual increase in the content of phosphate in the sludge water which reaches respectively 335 and 388 mg P/dm³, which is 59 and 68% of the gross amount of phosphorus. Continuous aeration is followed by oxidation of organic matter, including oxidation of cellular material itself, which explains the increase of phosphate concentration. So ash content of EAS after aerobic stabilization reached 31.2 and 31.3% for the air consumption of 40 and 54 m³/m³ · h respectively.

Aerobic stabilization at an air consumption of $54 \text{ m}^3/\text{m}^3 \cdot \text{h}$ is accompanied by a lowering of the pH value to 5.3, at an air consumption of $40 \text{ m}^3/\text{m}^3 \cdot \text{h}$ there is a slight decrease in the pH to 6.8. Perhaps a greater change in pH is due to the the nitrification process [19].

Conclusion. Prolonged anaerobic and aerobic stabilization of EAS lead to the release of phosphorus accumulated in the process of the biological treatment, from the solid phase of the sludge suspension. The greatest transition of phosphorus into sludge water, constituting 79% of the gross amount is observed in anaerobic processing mode without stirring. At aeration of EAS, phosphorus output depends on the air consumption and at 54 m³/m³ · h reaches 68% of its total content. In this regard, to reduce the load on the sewage treatment plant concerning phosphorus and return of valuable nutrients in the economic turnover, it is rational to connect it in the form accessible for using and to remove it from the sludge water produced while processing of EAS.

References

- 1. Cordell D., White S. Peak phosphorus: clarifying the key issues of a vigorous debate about long-term phosphorus security. *Sustainability*, 2011, vol. 3, no. 10, pp. 2027–2049.
- 2. Kuznetsov A. E., Gradova N. B. *Nauchnye osnovy ekobiotekhnologii* [The scientific basis of environmental biotechnology]. Moscow, Mir Publ., 2006. 504 p.
- 3. Cordell D., Rosemarin A., Schröder J. J., Smit A. L. Towards global phosphorus security: A systems framework for phosphorus recovery and reuse options. *Chemosphere*, 2011, no. 84, pp. 747–758.
- 4. Aloe A. K., Bouraoui F., Grizzetti B., Bidoglio G., Pistocchi A. JRC technical reports (Managing nitrogen and phosphorus loads to water bodies: characterisation and solutions towards macro-regional integrated nutrient management). Ispra, 2014. 89 p.
- 5. Anisimov D. V. Phosphorus removal from wastewater. *Ekologiya proizvodstva* [Manufactory ecology], 2012, no. 6, pp. 50–53 (in Russian).
- 6. Markevich R. M., Dubovik O. S., Lan'ko I. P. The dynamic of transformation of compounds of nitrogen and phosphorus in the wastewater during the biological treatment. *Trudy BGTU* [Proceedings of BSTU], 2014, no. 4, Chemistry, Technology of Organic Substances and Biotechnology, pp. 197–199 (in Russian).
- 7. Van Haandel A., Van der Lubbe J. Handbook of biological waste water treatment: design and optimization of activated sludge systems. Leidschendam, Quist Publ., 2007. 550 p.
- 8. Bol'shakov N. A. Minimization of secondary pollution during the process of wastewater treatment using technology of biological phosphorus removal. *Vodoochistka* [Water treatment], 2011, no. 12, pp. 6–9 (in Russian).
- 9. Sabliy L. A., Zhukova V. S., Kozar' M. Yu. Removal of nitrogen and phosphor in the complex for purification of wastewater and sedimentation treatment. *Vodoochistka* [Water treatment], 2014, no. 1, pp. 17–23 (in Russian).
- 10. Pupyrev E. I., Zakhvataeva N. V., Shelomkov A. S., Kozhushko A. Yu. Biogalvanic method to remove phosphor from wastewater. *Vodosnabzheniye i sanitarnaya tekhnika* [Water supply and sanitary technique], 2009, no. 8, pp. 55–59 (in Russian).
- 11. Shelomkov A. S., Zakhvataeva N. V. Removal of phosphor during wastewater treatment. *Voda* [Water], 2010, no. 8, pp. 13–15 (in Russian).
- 12. Lominoga O. A., Agapov D. V., Kell' L. S. Minimization of exudation of phosphorus content pollution during sludge wastewater treatment. *Vodosnabzheniye i sanitarnaya tekhnika* [Water supply and sanitary technique], 2013, no. 1, pp. 52–55 (in Russian).
- 13. Solov'eva E. A. Removal of nitrogen and phosphor in the complex for wastewater purifycation and sedimentation treatment. *Vodoochistka* [Water treatment], 2011, no. 4, pp. 41–58 (in Russian).
- 14. Kolbasov G. A., Nikolaev Yu. A. Problems of treatment of active sludge from plants fof biological removal of phosphorus. *Vodoochistka* [Water treatment], 2014, no. 2, pp. 30–36 (in Russian).
- 15. Harrison E. Z., McBride M. B., Bouldin D. R. Land application of sewage sludges: an appraisal of the US regulations. *Int. J. Environment and Pollution*, 1999, vol. 11, no. 1, pp. 1–36.

Ecology 205

16. STB ISO 6878-2005. Water quality. Determination of phosphorus. Ammonium molybdate spectrometric method. Minsk, Belorusskiy gosudarstvennyy institut standartizatsii i sertifikatsii Publ., 2006. 20 p.

- 17. TC WI:2003. Total phosphorus in soil, biowaste and sewage sludge. Date 08.2005. CEN/BT task Force 151 horizontal standards in the field of sludge, biowaste and soil. 16 p.
- 18. Kalyuzhnyy S. V., Danilovich, D. A., Nozhevnikova A. N. *Anaerobnaya biologicheskaya ochistka stochnykh vod* [Anaerobic biological wastewater treatment]. *The results of science and technology. Biotechnology.* Moscow, VINITI Publ., 1991, vol. 29, 182 p.
- 19. Karyukhina T. A., Churbanova I. N., Zaena I. Kh. *Sludge treatment and disposal*. Vol. 1. USA, Ohio, 1978. 236 p. (Russ. ed.: Karyukhina T. A., Churbanova I. N., Zaena I. Kh. *Obrabotka i udaleniye osadkov stochnykh vod*. Moscow, Stroyizdat Publ., 1985. 236 p.).

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