

# Methods for Removing of Phosphates from Wastewater

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**Abstract.** The paper offers update information on wastewater removal from phosphates. The writers describe the most commonly used efficient methods to remove phosphates from wastewater based on principles of biology, chemistry, physical chemistry and biological chemistry. The paper presents the results of research on phosphate-removing wastewater treatment methods using iron-bearing reinforced charge material.

## 1 Foreword

During the recent years, eutrophication processes have been posing as a serious threat for water bodies. Excess of biogenic substances coming from drainage areas deteriorates the quality of natural waters, and this generally causes changes in the structure of water body ecosystems. Overconcentration of biogenic substances triggers vigorous growth of cyanobacteriae, reduces dissolved oxygen content, suffocates fish populations, causes littoral overgrowth, and complicates water purification. Deteriorating quality of water in the water bodies is directly related to evolution of the processes of human-caused eutrophication. To resolve this complex issue, one needs to minimize biogenic discharge of nitrogen and phosphorus compounds into the waterbodies.

Limits for biogenic substance discharge into the water bodies have been made more rigorous in the Russian Federation (below 0.05 mgr/L for oligotrophic water reservoirs), and are much above the global standards effective at present. Urban wastewaters are the main contributor of biogenic components that enter water reservoirs. Right now, science researchers worldwide pay much attention to develop new and improve the available wastewater treatment methods to remove biogenic components. The issue of biogenic substance removal, phosphorus in particular, is a priority for higher quality of wastewater purification, and works towards improved ecology of the water environment to the greatest extent [1, 2].

## 2 Sources of Phosphates Entering Water Reservoirs

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To combat eutrophication of water reservoirs, one needs to identify the sources of phosphorus compounds that reach the water bodies.

Industrial and residential drains are the main source of phosphorus contaminating water reservoirs. Phosphates constitute an integral part of pollutants in such drains. Industrial and residential wastewaters contain phosphorus as a result of human excreta (30-50% of phosphorus comes with residential waters) and after wide use of synthetic detergents (50-70%) containing polyphosphate components.

The most common forms of phosphorus present in wastewaters are organic compounds, orthophosphates and polyphosphates. 70 to 90% of phosphorus in drain liquids is either orthophosphate or polyphosphate, which can get hydrolyzed up to orthophosphate. The rest of phosphorus is found as part of organic compounds.

The polluting load on water bodies can be reduced by preventing entry of biogenic components to wastewaters or by using more intensive treatment of such substances.

Most of phosphorus compounds found in wastewater are water soluble, and so mere precipitation can remove just a small fraction. Biological treatment uses biochemical processes to remove phosphorus, yet there is more phosphorus in water than any biochemical technology can handle. Therefore, primary and secondary wastewater treatment can remove about 20-30% of phosphorus, and phosphorus content in pre-treated water is high above standard regulated limits. Not all local water purification facilities have the phosphate removal ability, and so new technologies need to be designed to remove biogenic components from industrial and residential wastewaters.

There are numerous other ways how biogenic components enter water reservoirs:

- anthropogenic impact on topsoil by intensive agricultural chemistry methods (use of mineral fertilizers);
- creating water storage reservoirs over a large area with insufficient flow exchange;
- creating new water flows, mainly of wastewaters with high content of nitrogen and phosphorus compounds;
- developing industrial manufacturing facilities that generate more production wastewaters with biogenic components (production of mineral fertilizers and detergents); lots of biogenic components are found in food, land and cattle farming and wastewaters [1].

Small concentrations of biogenic components are present in rainwater's, but because the volume of rainwater's is great they strongly influence the composition of biogenic substances in the water reservoir. Considering that entry of rainwater to water reservoirs is brief, no strict requirements exist as regards removal of biogenic substances.

Industrial manufacturing companies are recommended to adopt water-free technologies or to build local purification facilities; facilities for industrial and residential wastewater treatment must implement advanced technologies that ensure maximized efficiency of phosphorus compound removal from wastewaters.

### **3 Removal of Phosphorus Compounds from Wastewater**

At present, there is a variety of ways to remove phosphates from liquid drains. Phosphates can be removed chemically (chemical and physical-chemical methods), biologically (the biological method) by modifying the biological process that incorporates phosphorus in the cellular substance, or by using the biological-chemical method.

Chemical and physical-chemical methods known to displace phosphorus are numerous and diverse. Chemical methods are generally avoided due to high cost of reagents and also because use of coagulants generates secondary pollution. Physical-chemical methods involve high expenditure of the processes and their complex use. Application of sorbents calls for thorough pre-treatment of the liquid drain, because presence of suspension dredge

and other pollutants in the water tend to compromise the sorptive capacity of materials, and this again makes purification processes more complex and expensive.

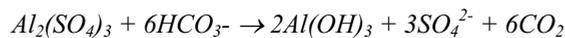
By now, the biological method of phosphorus removal is getting to be used universally. Conducted correctly, the process can remove phosphates efficiently, but in most cases it fails to achieve stable removal of phosphate from the drain fluid down to the regulated minimum concentration limit for fish farming reservoir water.

In practice, different patterns are used that combine biological processes with chemical precipitation. According to many researchers, this is the most promising combination that not only ensures higher quality of water purification compared to either single method, but also makes the process more stable. However, this method of phosphate removal from drain liquids also has certain disadvantages.

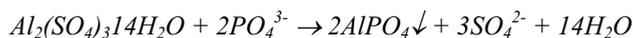
### 3.1 Chemical and Physical-Chemical Wastewater Treatment Methods to Remove Phosphorus Compounds

At this time, the chemical phosphorus removal method for wastewaters is both used and researched. This method has been widely used by small and medium-output plants.

During chemical purification of wastewater, the reagent ions interact with soluble salts of the orthophosphoric acid, thus creating highly dispersed colloid phosphate sediment. Meanwhile, the chemical reacts with water-borne bases to produce large-flake sediment. This sediment triggers coagulation of the high-dispersion colloid phosphate sediment and suspension, it also adsorbs some of the phosphorus-bearing organic compounds, and then it is withdrawn from the system. Salts of two- and three-valent metals are used as reagents. The practice of wastewater treatment widely uses such coagulants as aluminum and iron salts, and also lime. Adding aluminum sulfate to wastewater in the presence of alkali produces the following reaction:



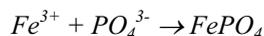
Further on, the following reaction occurs in the presence of phosphates:



These two reactions compete for aluminum ions, created by adding the reagent – aluminum sulfate. The flakes of aluminum hydroxide sediment absorb aluminum phosphates and colloid particles of solid impurities, thus helping to remove phosphorus by clearing out the wastewater.

The option was researched to use water line sediment to remove phosphorus compound from wastewaters; such sediment is produced when aluminum sulfate coagulates high-color low-turbidity waters as reagent.

When salts of three-valent iron are used as coagulant, the following reaction occurs:



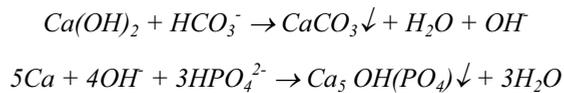
Used with green vitriol, two-valent iron is oxidized to three-valent iron:



FePO<sub>4</sub> particles in the sediment have colloid sizes, and so excess of ferric ions must be added in the quantity sufficient to produce iron hydroxide. The iron hydroxide sediment captures FePO<sub>4</sub> particles and other solid particles contained in wastewaters; in addition, it works as adsorbent in respect of other phosphorus-bearing compounds. Flaky sediment of

iron hydroxide is hard to precipitate, and frequently one needs to use organic polymers in order to produce clear supernatant water.

Use of lime as coagulant involves the following reactions:



Lime interacts with bicarbonate ions of wastewaters to produce calcium carbonate; in addition, it reacts with phosphates [4]. Orthophosphate is precipitated by calcium ions and produces calcium oxyapatite, while polyphosphates are removed through adsorption on pre-generated particles of calcium oxyapatite. As pH grows, solubility of calcium oxyapatite rapidly decreases, and removal of phosphorus improves. Virtually all orthophosphate precipitates at pH >9.5. At pH < 9.5, phosphorus is adsorbed on calcium carbonate.

Successful use of pelleted material manufactured of construction waste to purify phosphorus-bearing wastewaters is quite interesting; the results were quite positive [3].

By now, a whole series of physical-chemical methods are available that can remove phosphorus from wastewaters. Such methods include:

- adsorption method, where phosphorus is absorbed by the sorbent surface. Sorbent can be manufactured of granulated aluminum oxide, activated aluminum oxide, and aluminum sulfate, hydrated titanium dioxide, activated with oxides of Group 3 and Group 4 metals of the periodic system, with components coated on fiber materials; dolomite proved to have high adsorption ability respective to impurities of phosphorus compounds (with more than 95% of phosphorus removed). There is research of light bloating clays used to remove phosphorus from wastewaters, etc. Efficiency of phosphorus removal by this process can be quite high, rising to 100% in certain cases;

- method to remove phosphates in a magnetic field. Here, phosphates are bound with a reagent in insoluble compounds, whereupon magnetic material is added to create a magnetic field that isolates phosphate-containing sediment;

- electric coagulation and floatation treatment; this method can use electrodes of both aluminum and iron/steel, and also ensures total removal of phosphorus;

- crystallization method, based on growing phosphate crystals in wastewaters at crystallization centers later to be removed from the system; crystallization occurs on filters or in the suspended sludge.

However, none of the above physical-chemical methods has found wide practical application due to high costs needed to implement their processes, and relative complexity.

### **3.2 Biological Treatment Methods to Remove Phosphorus Compounds from Wastewater**

Biological methods that ensure best removal of phosphorus are of great interest, as they help to maximize the biological potential of activated sludge. The process of conventional biological purification removes only as much as 20 – 40% of phosphorus. Removal of phosphorus can be maximized to 50% by increasing the amount of sludge used, but this is not enough because up to 95% of phosphates must be removed to achieve the MPC level.

By now, there is a whole series of technologies available for biological removal of phosphorus, specifically: Phostrip, A/O (Anaerobic–Oxic), EASC (Extended Anaerobic Sludge Contact process), and other technologies.

To remove both phosphorus and nitrogen simultaneously from drain liquids, one can use systems such as UCT, Bardenpho, Phoredox, etc., with upgrades.

The UCT process is the most efficient method that removes phosphorus and nitrogen at the same time. In the UCT, recirculating sludge is directed from the secondary precipitation

tank to the anoxide zone, while part of the sludge mix returns from the anoxide zone to the anaerobic zone. In upgraded UCT systems, anoxide zones are subdivided into two sections.

Process updates mainly seek to reduce the effect of nitrates that are created in the aerobic process and remain in the system that holds concentrations of organic substances too low for the denitrification process [5].

The Bardenpho technology is graduated biological purification that includes alternating aerobic and anoxide zones where the sludge mix gets treated. The active sludge from the secondary precipitation tank and the first aerobic zone is recycled to the anoxide zone [6].

Apart from Bardenpho, all technologies include serially engaged anoxide, anaerobic, and aerobic zones in the wastewater treatment system. Organization of recirculation flows is a characteristic feature specific to all such systems.

In the Phoredox technology, active sludge from the secondary precipitation tank follows to the anaerobic zone, while the sludge mix from the aerobic zone returns to the first anoxide zone just as described in the above system.

### **3.3 Biological-Chemical Methods of Wastewater Treatment to Remove Phosphorus Compounds**

At present, a variety of systems is used practically that represent a match of a biological process and chemical precipitation. Such combination of processes achieves higher quality of purified water than if only one process used. Biological-chemical treatment systems differ by reagent sources and reagent compositions. Evolution of biological-chemical treatment processes goes along with that of reagents used to enable the process. The most promising are recently developed reagents made of manufacturing waste. This researches the option of sediments from water supply plants, extract of brown coal ashes, and manufacturing waste used as reagents. New reagents have been designed. Focus has also been on the reagent batching process.

During the biological-chemical treatment process, reagents can be added from different points. Thus, current facilities use the following systems for biological-chemical phosphate removal:

- prior removal of phosphorus at the mechanical treatment stage – this system can be used to purify high-concentration wastewaters, but it has a number of disadvantages: it needs greater amounts of reagent, thus increasing the amount of resulting sediment, and this makes the method more expensive;
- using reagent to treat biologically purified drain liquids – this system requires additional precipitation tanks, making the method more cost-intensive;
- reagent batching directly to the air tank (simultaneous precipitation) – the most rational way to use reagent for biological treatment; from experience, such systems improve sedimentation properties of activated sludge.

However, when the reagent is added to the system where a biochemical process is in progress, one must ensure that the rate of generating solid substances produced by chemical reagents does not exceed that of activated sludge in the biochemical process.

A promising way of phosphate removal is the biological corrosion or the biogalvanic method to remove phosphate from wastewater. We have researched this method in order to achieve higher efficiency of phosphate removal and deeper biological purification from organic contamination. The method is based on the principle that as living microorganisms in activated sludge oxidize organic substances they release acid products into the environment. Therefore, the contact line between the biofilm and wastewater creates a local zone where acid environment reaction occurs. When metal is introduced into the biofilm microsphere, the potential difference of the metal and solution triggers the electrochemical corrosion process, where metal ions pass into the solution and form insoluble salts with the

orthophosphoric acid ions [8,9,11]. It is known that ferric ions are beneficial for activated sludge, and that ferric ions  $\text{Fe}^{3+}$  strongly stimulate bacteria growth in activated sludge.

#### **4. Results of Biological Corrosion Method Research**

In the course of the research, reinforced feed material was placed inside an air tank. The feed material was reinforced with iron using Steel Grade 3 (low-carbon). The research continued for 6 months. A reference air tank with non-reinforced feed material was added and operated in parallel to compare the results.

The research demonstrated efficiency of phosphate removal to be around 60-70% for phosphate concentrations of some 14 mg/L in incoming drain waters. Meanwhile, it was observed that purification of organic contamination was considerably higher. After the reinforced feed material was placed in the air tank, the efficiency of phosphate removal rose to 99%, but decreased to  $\approx 60\%$  after 15 days. We also need to note that the amount of free-floating activated sludge increased from  $\approx 2.0$  g/L (using non-reinforced feed material) to  $\approx 4.0$  g/L. The sludge index decreased in reverse proportion to the increase of sludge.

These changes in sludge amount, sludge index and efficiency of phosphate removal can be explained by dramatically higher concentration of dissolved total iron in the air tank after the reinforced feed material was placed there.

As they react with phosphates, ferric ions produce basic iron phosphate (2 and 3) and iron orthophosphate (2) octahydrate. At the same time, a reaction producing iron hydroxide occurs, which adsorbs phosphates and other solid particles of various origin; in addition, it acts as an adsorbent for other phosphorus-bearing compounds. In turn, activated sludge that remains in suspension adsorbs hard-to-precipitate particles of iron hydroxide, and thus makes sludge flakes heavier and larger. Subsequently, a biological film forms on the feed material, while the surface of the filling iron receives a film of iron oxide and iron phosphate, so concentration of dissolved iron drops to a near-zero value or at least below the content of iron in the incoming drain liquid; these processes lower the effect of treatment for phosphates.

Comparing the results of air tank operation using reinforced and reference feeds produced a biological process activation ratio of 1.78, which was evidence of a much more intensive treatment process to remove organic contamination with reinforced feed material.

#### **5 Conclusions**

It has been demonstrated that the biological corrosion method is highly efficient to remove phosphates from wastewaters. Based on the research, one can conclude that reinforced feed material boosts the efficiency of phosphate removal from wastewater, and can enhance processes that remove both phosphates and organic contamination from wastewater. This purification method can be recommended to be used not only to raise the efficiency of phosphate removal, but also to achieve in-depth biological treatment of wastewater in general.

#### **References**

1. M. Shourian, A. Moridi, M. Kaveh, *Water Sci. and Technol.*, **74** (6) 1376-1385 (2016) DOI: 10.2166/wst.2016.322 (2016)
2. G. Li, F. Xie, J. Zhang, J. Wang, Y. Yang, R. Sun, *Water Sci. and Technol.*, **74** (6) 1266-1273 (2016) DOI: 10.2166/wst.2016.277 (2016)

3. Sh. Yang, P. Jin, X. C. Wang, Q. Zhang, X. Chen, *Water Sci. and Technol.*, Available Online 10 January 2017, wst2017019; DOI: 10.2166/wst.2017.019 (2017)
4. Ch. Han, Z. Wang, Q. Wu, W. Yang, H. Yang, X. Xue, **73 (7)** 1644-1651 (2016) DOI: 10.2166/wst.2015.642
5. A. G. Kapagiannidis, I. Zafiriadis, A. Aivasidis, **60 (10)** 2695-2703 (2009) DOI: 10.2166/wst.2009.703
6. S. Puig, Ll. Corominas, M.D. Balaguer, J. Colprim, **55 (7)** 135-141 (2007) DOI: 10.2166/wst.2007.137
7. R. Rodríguez-Gómez, G. Renman, **73 (12)** 2959-2970 (2016) DOI: 10.2166/wst.2016.162 (2016)
8. O.A. Ruzhitskaya, E.S. Gogina, *Advanced Materials Research*, **919-921**, 2153-2156, (2014) DOI:10.4028/www.scientific.net/AMR.919-921.2153
9. O.A. Ruzhitskaya, E.S. Gogina, *Advanced Materials Research*, **919-921**, 2141-2144 (2014) DOI:10.4028/www.scientific.net/ AMR.919-921.2141,
10. N. Zaletova, Y. Voronov, N. Makisha, *International Journal of Applied Engineering Research*, **10(21)**, 42454-42455 (2015)
11. O. Ruzhitskaya, O. Yantsen, *International Journal of Applied Engineering Research*, **11(5)**, 3496-3498, (2016)
12. H. Jae-Hoon, Ch. Jared, L. Seung-Jin, P. Jungsu, and L. Woo Hyoung. *Environmental Engineering Science*, **33(11)**, 882-897 (2016) DOI:10.1089/ees.2016.0132
13. Y. Yang, F. Tang, X. Su, H. Yin, F. Ge, *Water Sci. and Technol.*, Published December 2016, **74 (11)** 2727-2735; DOI: 10.2166/wst.2016.437 (2016)
14. R. Xie, Y. Chen, T. Cheng, Y. Lai, W. Jiang, Zh. Yang, **73 (8)** 1891-1900 (2016) DOI: 10.2166/wst.2016.021
15. H. Wang, Zh. Zou, X. Xiao, D. Chen, K. Yan, **73(11)**, 2689-2696 (2016) DOI:10.2166/wst.2016.106