Phosphate removal from wastewater using reinforced feed material at the tertiary treatment stage

Olga Ruzhitskaya
Peoples’ Friendship University of Russia (RUDN University), Department of Civil Engineering, 6 Miklukho-Maklaya St., Moscow, 117198, Russia
E-mail: ruzhitskaya-oa@rudn.ru

Abstract. In recent years, eutrophication processes have posed a serious threat to water bodies. As a result of excess inputs of nutrients (nitrogen and phosphorus) from drainage basins, natural water quality deteriorates, which is usually accompanied by changes in the water bodies ecosystem structure. The increased concentration of nutrients leads to the rapid development of blue-green algae, reduced dissolved oxygen, fish-kill, coastal zones overgrowth, treated water processing complication. The article provides relevant information in the field of phosphate-removing wastewater treatment. The article presents advanced chemical and physical-chemical methods of phosphate-removing wastewater treatment. The article presents the results of the research on phosphate-removing wastewater treatment methods using iron-bearing feed material. The evidence of physical-chemical nature of deep phosphate-removing purification of water is presented. Deep phosphate removal is mainly due to physical-chemical processes of phosphate coagulation with ferrous ions, the source of which is the metal in the feed material, which is subjected to processes of electrochemical corrosion. When the biofilm loading becomes overgrown, the contact of the metal surface area with water decreases and the purification effect decreases. After regeneration of the load, the efficiency of phosphate removal increased to its previous level. Using the method of deep phosphate removal from domestic wastewater, with the help of reinforced feed material, at the tertiary treatment stage the required efficiency of phosphate removal can be achieved, however, there is a high consumption of metal in the feed material.

1. Foreword
In recent years, eutrophication processes have posed a serious threat to water bodies. As a result of excess inputs of nutrients (nitrogen and phosphorus) from drainage basins, natural water quality deteriorates, which is usually accompanied by changes in the water bodies ecosystem structure. The increased concentration of nutrients leads to the rapid development of blue-green algae, reduced dissolved oxygen, fish-kill, coastal zones overgrowth, treated water processing complication.

Industrial and residential wastewater is the main source of phosphorus contaminating water bodies. Phosphates are 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.

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 removes about 20–30 % of phosphorus, and phosphorus content in pre-treated water is high above standard regulated limits.

There is a great variety of ways to remove phosphates by chemical and physical-chemical methods. The chemical method is complicated by high cost of reagents and also because the 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 drain liquid, because the presence of suspended substances and other pollutants in the water tends to compromise the sorptive capacity of materials, and this again makes purification processes more complex and expensive.

At present, the research of chemical phosphorus removal method for wastewater continues. 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.

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

− Adsorption method, where phosphorus is absorbed by the sorbent surface.
− 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. This method 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.

The successful use of granular material made of construction waste for phosphorus-containing treatment wastewater is interesting; the use of such material has shown positive results (1).

Israeli scientists have studied the possibility of removing phosphates from the secondary synthetic effluent by adsorption on iron oxide agglomerations (IOAs) in an immersion membrane reactor, while studying its regeneration and reuse. The use of iron oxide (IOAs) as a renewable adsorbent has demonstrated its high adsorption capacity, which has consistently maintained its sorption capacity after regeneration (at the fifth adsorption cycle 93 % of the original adsorption capacity was obtained). The adsorbent proposed by Israeli scientists has the potential to be used in phosphate-removing wastewater treatment (2).

The new adsorbent La-biochar has shown high phosphate adsorption capacity – 36.06 mg R/g, pH compatibility from 3 to 12, favorable selectivity for phosphate among other ions, effective desorption of 92.3 % with preserved adsorption capacity of 85 % after 5 cycles (3).

Membrane Capacitive Deionization (MCDI) is a novel technology for the effective purification of water, including domestic wastewater. Main technological parameters for successful phosphate-removing water treatment are given in the work of South Korean scientists (4).

US and Chinese scientists have carried out the joint research to develop a migration electric-field assisted electrocoagulation (MEAEC) system to increase phosphate removal from domestic wastewater, with reduced energy consumption (5).

The global scientific agenda for phosphate removal from wastewater is mainly aimed at finding and investigating new materials that can be successfully applied as adsorbents and at the same time be available and inexpensive, have good adsorption properties, maintain the quality of treatment after multiple adsorbent regenerations. In recent years, various materials have been studied: magnetic
adsorbent – alloyed spent liquid catalysts for catalytic cracking (6), mesoporous silica modified with lanthanum oxide (7), nanospherical calcium carbonate obtained from solid waste (8), the use of waste mollusk shell (9), zirconium-modified zeolite (10), ferrihydrite-coated and lanthanum-decorated magnetite (11), the use of acid-activated akadama clay (12), investigation on phosphate removal from aqueous solutions using iron oxides (13), the application of thermally treated bentonite (B800) as an adsorbent for low-concentration phosphorus removal from wastewater (14), investigation on adsorption capacity for phosphate in wastewater from thermally activated fly ash desulfurization gypsum (15), a hybrid adsorbent of nanoscale zirconium molybdate embedded in a macroporous anion exchange resin (ZMAE) for the selective removal of phosphate (16), investigation on mechanism of phosphate removal on carbonized sludge adsorbent (17), phosphate adsorption on iron-modified biochars derived from waste activated sludge (18), investigation on bentonite-lanthanum clay as an adsorbent for highly concentrated wastewater treatment (19), use of Na-P1 zeolite synthesized from coal fly ash (20).

2. Investigation of the possibility of deep phosphate removal from domestic wastewater using reinforced feed material at the tertiary treatment stage

In order to determine the possibility of phosphate removal from wastewater with low loads of organic substances by means of reinforced feed material, investigations were carried out in the flow mode using the technological scheme with tertiary treatment of biologically treated wastewater, consisting of an air tank, precipitation tank, post-treatment bioreactor and tertiary precipitation tank. A steel-wire reinforced feed material was installed in the post-treatment bioreactor.

The time of the waste liquid in the pre-treatment bioreactor was being changed from 2 to 6 hours. To determine the impact of critical loads on bioreactor operation, aeration time was reduced to 40 minutes and increased to 15 hours. The post-treatment bioreactor was working without the return of activated sludge. To determine the effect of feed material regeneration on the phosphate removal effect, the feed material was flushed. In order to determine the optimum regeneration interval, the flushing was performed at different intervals. The research has lasted for 6 months until stable results were achieved.

The content of phosphates in the wastewater incoming into the bioreactor varied from 2 to 16 mg/l, ammonium nitrogen from BLD to 20 mg/l, BOD5 from concentrations below the limit of detection to 20 mg/l and suspended substances from 1.5 to 57 mg/l. The concentration of phosphate in the wastewater incoming into the bioreactor was on average 4–6 mg/l, while studying the effect of phosphorus slug loads reached 16 mg/l.

2.1. The results and analysis of the post-treatment bioreactor with reinforced feed material operation

Sanitary and chemical analyses have confirmed the possibility of effective phosphate removal from discharge liquid when using reinforced feed material at the tertiary treatment stage. After the reinforced feed material was placed into the bioreactor, the effective phosphate removal was carried out in the first 20 days after installation. During the same period, an increased concentration of total dissolved iron in the reactor was observed, which reached 3 mg/l. The phosphate removal efficiency was then destabilized and varied between 30 and 60 %. Similarly, the concentration of total dissolved iron also varied from BLD to 0.5 mg/l.

It was noted that the efficiency of phosphate removal decreased as the biofilm load was overgrown, the more microflora attached to the load, the less total dissolved iron was detected in the bioreactor and the less phosphate removal effect was observed. After the regeneration of the load, the efficiency of phosphate removal increased to the same level, but the concentration of dissolved iron in the bioreactor increased.

The studies have shown that phosphate removal is mainly due to physical-chemical processes of phosphate coagulation with ferrous ions, the source of which is the metal in the feed material, which is subjected to processes of electrochemical corrosion. When the biofilm loading becomes overgrown, the contact of the metal surface area with water decreases and the purification effect decreases.
Continuous aeration increases the dissolved oxygen content in the bioreactor, which in turn speeds up corrosion processes. If there is a high content of dissolved oxygen in the water, which is typical for small values of BOD of the incoming waste liquid, even at moderate intensity of aeration, a film is formed on the metal, which protects the metal from corrosion and thus reduces the effect of phosphate cleaning.

After the feed material regeneration (high pressure flushing with water) the cleaning efficiency is restored, therefore one can assume that the reduction of the effect is not due to the protective film on the metal, but to the biological film formed on the feed material, as it is impossible to remove the protective film during flushing. It is likely that after regeneration (until the biological film is formed on the feed material) a protective film is being formed on the metal. Biological film microorganisms formed in the future corrode the protective film and when it is washed off during the flushing, the surface of the metal is released from corrosion products, and the intensity of corrosion is resumed. By stimulating the intensity of corrosion, iron consumption is also stimulated. Thus, the number of steel wires in the load has decreased by 61.6 % since the beginning of the experiment.

The conducted research has allowed to see the dependence between a specific surface of a steel wire of a loading material and efficiency of phosphate removal. The more metal is in the feed material, the greater is the effect of phosphate removal (Fig. 1).

![Figure 1](image.png)

**Figure 1.** The dependence between the degree of phosphate removal and the specific surface of the steel wire of the feed material in the bioreactor.

The dependence between the duration of aeration and the efficiency of phosphate removal has been revealed. It was found that with the same amount of metal in the feed material, the longer is the aeration, the greater is the effect of phosphate removal (Fig. 2).
Figure 2. The dependence between the phosphate removal efficiency and the duration of aeration.

Together with the decrease in phosphate concentration, there is a decrease in contamination on such indicators as BOD5 and suspended substances. In the process of the research, the influence of reinforced feed material on the second stage of nitrification and ammonium nitrogen reduction was established.

The main data of the experiment (with aeration duration of 4–6 hours) are given in Table 1.

| Parameters, mg/L                  | Incoming drain liquids | Treated drain liquids |
|----------------------------------|------------------------|-----------------------|
| Phosphates                       | 2–6                    | BLD* – 1              |
| Iron                             | BLD* – 0.3             | BLD* – 0.2            |
| BOD₅                             | 5–20                   | BLD* – 10             |
| Ammonium nitrogen                | BLD* – 20              | BLD* – 16             |
| Nitrites                          | BLD* – 17              | BLD* – 21             |
| Nitrates                         | 2–18                   | 2.5–18                |
| Suspended substances             | BLD* – 25              | BLD* – 10             |

BLD* – below the limit of detection

3. Conclusions

Today, in contrast to chemical methods, physical and chemical methods are increasingly being used in the practice of phosphate-removing wastewater treatment. From all physical-chemical methods, the adsorption method, in which phosphorus is absorbed by sorbent surface, has received the greatest distribution. New materials with high sorption capacity and economic efficiency are being developed, but the issue of processes implementation complexity remains unsolved. Using the method of deep phosphate removal from domestic wastewater, with the help of reinforced feed material, at the tertiary treatment stage the required efficiency of treatment can be achieved, however, there is a high consumption of metal in the feed material.
References

[1] Shengjiong Yang, Pengkang Jin, Xiaochang C. Wang, Qionghua Zhang, Xiaotian Chen «Phosphorus removal from aqueous solution using a novel granular material developed from building waste» Water Sci. and Technol., Available Online 10 January 2017, wst2017019; DOI: 10.2166/wst.2017.019 (2017)

[2] Shemer, H., Armush, A., Semiat, R. (2019). Reusability of iron oxyhydroxide agglomerates adsorbent for repetitive phosphate removal. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 579 doi:10.1016/j.colsurfa.2019.123680

[3] Xu, Q., Chen, Z., Wu, Z., Xu, F., Yang, D., He, Q., Chen, Y. (2019). Novel lanthanum doped biochars derived from lignocellulosic wastes for efficient phosphate removal and regeneration. Bioresource Technology, 289 doi:10.1016/j.biortech.2019.121600

[4] Jiang, J., Kim, D. I., Dorji, P., Phuntsho, S., Hong, S., Shon, H. K. (2019). Phosphorus removal mechanisms from domestic wastewater by membrane capacitive deionization and system optimization for enhanced phosphate removal. Process Safety and Environmental Protection, 44-52. doi:10.1016/j.psep.2019.04.005

[5] Tian, Y., He, W., Liang, D., Yang, W., Logan, B. E., Ren, N. (2018). Effective phosphate removal for advanced water treatment using low energy, migration electric–field assisted electrocoagulation. Water Research, 138, 129-136. doi:10.1016/j.watres.2018.03.037

[6] Yuan, L., Qiu, Z., Yuan, L., Tariq, M., Lu, Y., Yang, J., Lyu, S. (2019). Adsorption and mechanistic study for phosphate removal by magnetic Fe3O4-doped spent FCC catalysts adsorbent. Chemosphere, 183-190. doi:10.1016/j.chemosphere.2018.11.132

[7] Jia, X., He, X., Han, K., Ba, Y., Zhao, X., Zhang, Q. (2019). La2O3-modified MCM-41 for efficient phosphate removal synthesized using natural diatomite as precursor. Water Science and Technology, 79(10), 1878-1886. doi:10.2166/wst.2019.186

[8] Deng, S., Chen, Y. (2019). A study by response surface methodology (RSM) on optimization of phosphorus adsorption with nano spherical calcium carbonate derived from waste. Water Science and Technology, 79(1), 188-197. doi:10.2166/wst.2019.048

[9] Souza, T. A., Mascarenhas, A. J. S., Andrade, H. M. C., Santos, T. S. M. (2018). Combining sewage sludge and clam shell waste to prepare adsorbents for efficient phosphorous removal. Water, Air, and Soil Pollution, 229(12) doi:10.1007/s11270-018-4029-1

[10] Yang, J., Yang, M., Gui, H., Li, G., Wang, H. (2018). Dynamic and static adsorption of phosphate in water on the zirconium oxychloride modified zeolite. Desalination and Water Treatment, 135, 408-417. doi:10.5004/dwt.2018.23157

[11] Fu, H., Yang, Y., Zhu, R., Liu, J., Usman, M., Chen, Q., He, H. (2018). Superior adsorption of phosphate by ferrihydrite-coated and lanthanum-decorated magnetite. Journal of Colloid and Interface Science, 530, 704-713. doi:10.1016/j.jcis.2018.07.025

[12] Wang, Y., He, H., Zhang, N., Shimizu, K., Lei, Z., Zhang, Z. (2018). Efficient capture of phosphate from aqueous solution using acid activated akadama clay and mechanisms analysis. Water Science and Technology, 78(7), 1603-1614. doi:10.2166/wst.2018.441

[13] Ajmal, Z., Muhmood, A., Usman, M., Kizito, S., Lu, J., Dong, R., Wu, S. (2018). Phosphate removal from aqueous solution using iron oxides: Adsorption, desorption and regeneration characteristics. Journal of Colloid and Interface Science, 528, 145-155. doi:10.1016/j.jcis.2018.05.084

[14] Chen, X., Wu, L., Liu, F., Luo, P., Zhuang, X., Wu, J., Xie, G. (2018). Performance and mechanisms of thermally treated bentonite for enhanced phosphate removal from wastewater. Environmental Science and Pollution Research, 25(16), 15980-15989. doi:10.1007/s11356-018-1794-8

[15] Cheng, P., Chen, D., Liu, H., Zou, X., Zhang, Y., Xie, J., Chen, T. (2018). Enhanced adsorption capacity for phosphate in wastewater from thermally activated flue gas desulfurization gypsum. Journal of Chemical Technology and Biotechnology, 93(6), 1733-1741. doi:10.1002/jctb.5546
[16] Bui, T. H., Hong, S. P., Yoon, J. (2018). Development of nanoscale zirconium molybdate embedded anion exchange resin for selective removal of phosphate. Water Research, 134, 22-31. doi:10.1016/j.watres.2018.01.061

[17] Zhang, L., Liu, J., Guo, X. (2018). Investigation on mechanism of phosphate removal on carbonized sludge adsorbent. Journal of Environmental Sciences (China), 64, 335-344. doi:10.1016/j.jes.2017.06.034

[18] Yang, Q., Wang, X., Luo, W., Sun, J., Xu, Q., Chen, F., Zeng, G. (2018). Effectiveness and mechanisms of phosphate adsorption on iron-modified biochars derived from waste activated sludge. Bioresource Technology, 247, 537-544. doi:10.1016/j.biortech.2017.09.136

[19] Kurzbaum, E., Raizner, Y., Cohen, O., Rubinstein, G., Bar Shalom, O. (2017). Lanthanum-modified bentonite: Potential for efficient removal of phosphates from fishpond effluents. Environmental Science and Pollution Research, 24(17), 15182-15186. doi:10.1007/s11356-017-9116-0

[20] He, H., Xu, S., Han, R., Wang, Q. (2017). Nutrient sequestration from wastewater by using zeolite Na-P1 synthesized from coal fly ash. Environmental Technology (United Kingdom), 38(8), 1022-1029. doi:10.1080/09593330.2016.1217061