

## **EVALUATION OF SEWAGE SLUDGE BIOCHAR USE IN WASTEWATER TREATMENT FROM PHOSPHATE**

Judita Paulionytė<sup>1</sup>, Rasa Vaiškūnaitė<sup>2</sup>, Aušra Mažeikienė<sup>3</sup>

*Department of Environmental Protection and Water Engineering, Environmental Engineering Faculty,  
Vilnius Gediminas Technical University*

E-mail: <sup>1</sup>judita.paulionyte@stud.vilniustech.lt<sup>1</sup>; rasa.vaiskunaite@vilniustech.lt <sup>2</sup>; ausra.mazeikiene@vilniustech.lt <sup>3</sup>

**Abstract.** Phosphorus is important in the environment and its recovery and recycling is necessary. Sewage wastewater is one of the substances in which a high amount of phosphorus and its compounds are found. Phosphorus in water is one of the causes of environmental problems such as eutrophication. The utilization of sewage sludge is a main problem in both large and smaller towns. This research investigates how much and how to use sewage sludge biochar as an adsorbent to remove phosphorus compounds from wastewater. This article highlights the sorption capacity of the filler to absorb phosphorus compounds.

**Keywords:** biochar, sludge ash, phosphate, adsorption, wastewater, sewage sludge, phosphate treatment, phosphorus

### **Introduction**

Sewage sludge is formed by treating different types of waste water. One of them is household water and waste which comes from households, while the other, so-called industrial wastewater, is collected from industrial facilities. In the United States of America, China and India every year around 12.7, 7.8 and 4.0 million dry tonnes of municipal sludge must be properly disposed of by the requirements (Liu et al., 2021). Sewage sludge contains a number of harmful substances such as heavy metals, petroleum products, and chemical detergents. Recently, waste-related questions to sewage sludge treatment have become a major concern, whereas their disposal in landfills is undesirable and the management of this waste is a prohibited practice. Lithuania has already begun to apply good practices for the return of sewage sludge to the circular economy. However, only small amounts of sludge are composted in Europe and more energy-efficient uses are applied, such as the production of biofuels or incineration (Lietuvos socialinių mokslų centro Ekonomikos ir kaimo vystymo institutas, 2020). Lithuania follows this use, clearly understanding that sludge composting is not the best practice.

The utilization of sewage sludge is the main problem in both large and smaller towns. In larger cities, the

sludge is treated in sludge treatment facilities located in the same areas as water management companies, while smaller cities are forced to transport the resulting sludge to designated locations. Probiotics, which are unfortunately expensive, must be used regularly to prevent odours from spreading.

Stricter requirements for wastewater are the protection of the environment from pollution and the fight against the main natural problem - eutrophication. The efficiency of the treatment of water contaminated with nitrogen and phosphorus in small wastewater treatment plants is limited. The result of the biological treatment of wastewater contaminated with phosphorus compounds is excess sludge with high phosphorus content. As the efficiency of wastewater treatment improves, the amount of sewage sludge increases and accumulates; for example, the amount of sludge per 100,000 inhabitants in a sewage treatment plant can reach about 1825 t of dry matter per year (Lietuvos socialinių mokslų centro Ekonomikos ir kaimo vystymo institutas, 2020). One of the methods is to perform experimental studies that would evaluate the possibilities of using sewage sludge biochar in the treatment of wastewater from phosphates so that incompletely treated wastewater does not harm the environment.

A high concentration of phosphorus in water is one of the causes of environmental problems. Due to this, the political and economic sectors created a phosphorus recovery and recycling strategy that was considered to be able to meet future phosphorus demands. Therefore, environmental requirements are tightened, and the Wastewater Management Regulation came into force in 2006. According to which phosphorus compounds from wastewater (up to 5 mgP/l) are mandatory in small wastewater treatment plants (which treat up to 5 m<sup>3</sup> of wastewater per day) (Lietuvos Respublikos aplinkos ministerija, 2006). The removal of phosphorus from wastewater is possible by combining phosphates into a solid phase that can be separated from water. Such processes include chemical precipitation and biological phosphate removal. Both methods can achieve 80–90% phosphorus removal (Sincero, A. P., Sincero G. A., 2003).

In most of studies, sewage sludge biochars were used as in the agricultural and energy industries (Callegari et al., 2018; Fang et al., 2018; Figueiredo et al., 2017; Karim et al., 2019; Nobaharan et al., 2021; H. Wang et al., 2020; Yang et al., 2018; Yin et al., 2019). However, more scientists started to investigate the opportunities of biochar from sewage sludge as secondary material and gain a more important role as an adsorbent (Gopinath et al., 2021; Singh et al., 2020). The following properties of sewage sludge biochar are being studied around the world: composition of elements (Figueiredo et al., 2017), distribution of trace elements in biochar (Chen et al., 2020), and sorption properties (Callegari et al., 2018; Ma et al., 2020).

The experiment performed and the results of it allow us to determine whether biochar from sewage sludge can be produced as biochar and used to remove phosphates from wastewater. The efficiency of biochar adsorption of phosphates will be determined by using different initial concentrations.

The aim of the study was to investigate the application of sewage sludge biochar to the removal of phosphate from wastewater and the parameters influencing its efficiency.

## Methodology

The experimental research work was performed with artificially contaminated deionized water by different concentrations of phosphate.

The aim of the experimental research was to determine the phosphate adsorption on biochars. Experimental studies were performed with different phosphate concentrations and fixed sewage biochar mass.

The adsorbent was sewage sludge ash that was pyrolyzed. Municipal sewage sludge was taken from a municipal wastewater treatment plant which was located in

Vilnius city (Lithuania). Biochar was prepared by pyrolysis in a tube furnace method (Januševičius et al., 2022). The pyrolysis was chosen to temperatures of 300 °C, 400 °C, 500 °C, and 600 °C.

The potassium dihydrogen orthophosphate (KH<sub>2</sub>PO<sub>4</sub>) was dissolved in deionized water to make the desired phosphate stock solution. Two different adsorption solutions of phosphate concentrations were prepared: 50 mg/l and 100 mg/l. These phosphate concentrations were selected based on previous research (J. Li et al., 2019; Z. Wang et al., 2021; Yin et al., 2019). All test substances, chemical reagents, and mixtures used in the experiment were analytical grade.

A 1 g portion of each type of sewage sludge biochar sample was added into each prepared solution. After mixing, the bottle cap was closed and rotated end-to-end at 11 rpm for 2 h.

After that, the samples were filtered using gravity filtration. Furthermore, the determination of pH of filtered samples has been measured using a pH meter.

The samples were then measured using the colorimetry method to determine the concentration of phosphate after the process of absorption. The amount of adsorbate adsorbed by biochar equilibrium was calculated according to Equation (1):

$$q_e = V \times \frac{(c_e - c_0)}{m} \quad (1)$$

Where  $q_e$  (mg/g) is the equilibrium adsorption capacity which is the amount of adsorbate adsorbed per gram of biochar,  $V$  is the volume of solution,  $c_e$  and  $c_0$  represent the concentrations at the initial and final time (mg/l), respectively, and  $m$  is the weight of biochar (adsorbent) (g).

By using the initial and final phosphate concentrations in solutions was used to calculate the removal efficiency (%).

The experimental results were indicated as mean ± standard deviation. The average was calculated from three replicates of each experimental treatment. The analysis of the variance of data was performed and only acceptable values were chosen when the p-value was less than 0.05.

## Results

To characterize the relationship between the adsorption capacity of biochar and the concentration of the adsorption solution, a comparison between two different initial phosphate concentrations and four biochar pyrolysis temperatures were chosen to analyze.

The porous structure and specific surface area of biochar play an important role in adsorption (Agrafioti

et al., 2013; Hossain et al., 2011; Januševičius et al., 2022; Lu et al., 2013; Yin et al., 2019). On this basis, the variation of the chosen sewage sludge biochar pyrolysis temperatures was used to determine the effectiveness of adsorption.

The removal efficiency of phosphate by different biochar pyrolysis temperatures varies, as shown in Fig. 1, Fig. 2. The equilibrium adsorption capacity of phosphate by different biochars pyrolysis temperatures vary, as shown in Fig. 3, Fig. 4.

The results of biochar 300 °C absorption of phosphate at 50 mg/l were lower than dry sludge granules. The performance of biochar 300 °C may have been affected by the fact that during the pyrolysis process at 300 °C, not all organic compounds were turned into carbon. Furthermore, most researchers conclude that sewage sludge biochar produced at low temperatures (300 °C, 400 °C) may have a higher chance of total and total organic carbon and nitrogen content, but a lower total Na, P, and K contents (Khanmohammadi et al., 2015). Furthermore, by increasing the pyrolysis temperature, the percentage of C, O, H, and N generally decreases (Gopinath et al., 2021). It should be noted that this result will not be discussed or analyzed in this article due to previously mentioned factors.

The highest adsorption efficiency of phosphate was recorded in samples: at a concentration of 100 mg/l, the equilibrium adsorption efficiency of 6 mg/g was recorded and a concentration of 50 mg/l, the equilibrium adsorption efficiency of 2,6 was observed.

It should be noted that in solutions with a concentration of 100 mg/l of phosphate ions with biochar 400 °C, 500 °C, 600 °C temperature the equilibrium adsorption capacity and removal efficiency were slightly changed by increasing only from 5 mg/g to 6 mg/g and 50 % to 60 % values, was recorded in all samples.

Previous studies have confirmed that the biochar efficiency can reach up to 20 mg/g (J. Li et al., 2019) or using co-pyrolysis 50 mg/g adsorption of phosphate (Yin et al., 2019). In this research the existence of low absorption values in most of the samples could have been due to a large amount of organic elements left in the biochar, this also has been shown in other studies (Chen et al., 2020; Khanmohammadi et al., 2015) or it could have been due to the amount of biochar used. On the other hand, some researchers even used lower amounts of biochar to absorb other ions (Yang et al., 2018; Yin et al., 2019).

Meanwhile, when evaluating and comparing the equilibrium adsorption capacity (mg/g) of the control samples between two different phosphate initial concentrations, it was observed that at 50 mg/l the adsorption efficiency slightly decreased compared to 100 mg/l.

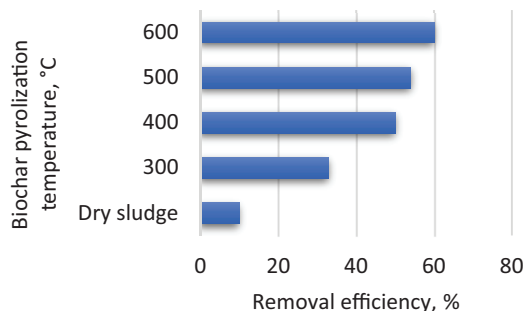


Figure 1. Graph of the the dependence of phosphate removal efficiency on the different sewage sludge biochar pyrolysis temperatures when the initial concentration of phosphate is 100 mg/l

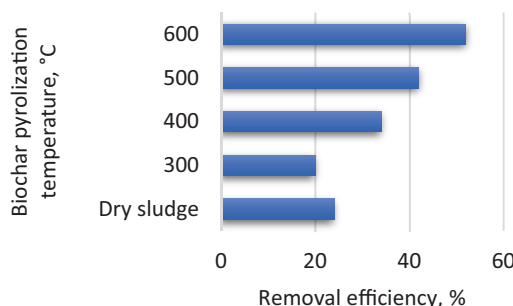


Figure 2. Graph of the the dependence of phosphate removal efficiency on the different sewage sludge biochar pyrolysis temperatures when the initial concentration of phosphate is 50 mg/l

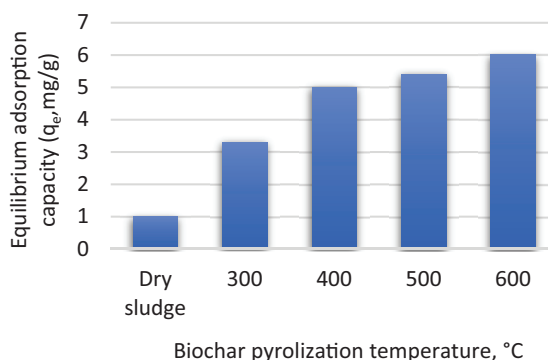


Figure 3. Graph of phosphate equilibrium adsorption capacity dependence on the different sewage sludge pyrolysis temperatures when the initial concentration of phosphate is 100 mg/l

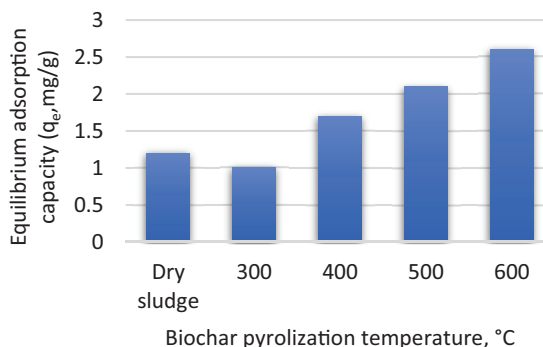


Figure 4. Graph of phosphate equilibrium adsorption capacity dependence on the different sewage sludge biochar pyrolysis temperatures when the initial concentration of phosphate is 50 mg/l

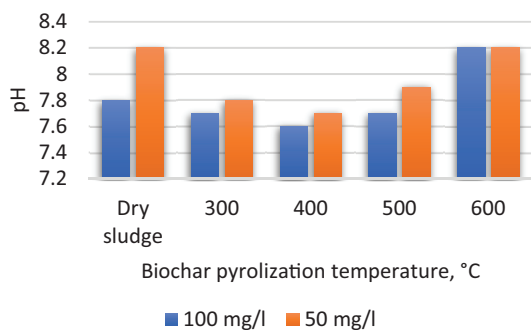


Figure 5. Graph of the pH value after adding sewage sludge biochar and removal of phosphate

Therefore, the comparison when evaluating and comparing the removal efficiency (%) of control samples between two different phosphate initial concentrations, it was observed that at 50 mg/l the adsorption efficiency decreased by double compared to 100 mg/l. It can be assumed that using sewage sludge ash, sewage sludge biochar made at 300 °C temperature is not sufficient to ensure larger changes in adsorption efficiency.

As mentioned before the pH values were determined after phosphate sorption to determine the effects of sewage biochar on water and identify possible initial pH values for another upcoming research. The results are shown in Fig. 5. The initial phosphate solution pH value was 6.8. In all samples, the pH value increased after adding sewage sludge biochar to solutions.

Studies have shown that with an increase in pH in samples, higher values of equilibrium adsorption capacity and removal efficiency were recorded (one exception was observed). Meanwhile, when comparing the different initial phosphate concentration of pH values, it was found that the higher the pH value, the higher the sorption capacity values were recorded (highest values with 600 °C pH = 8.2,  $q_e = 6$  (at 100 mg/l) and  $q_e = 2.6$  (at 50 mg/l)). The pH of the solution increases because sewage sludge pyrolysis at 600 °C increases the concentration of alkali metals (Januševičius et al., 2022). Therefore, the higher the temperature of the pyrolyzed sludge, the higher its pH.

Based on the data presented in Fig. 1, Fig. 2, Fig. 3, and Fig. 4, it can be concluded that, with increasing sewage sludge pyrolysis temperature, a significant increase in adsorption efficiency is observed. In conclusion, sewage sludge biochar makes it a promising sorbent for phosphate removal from wastewaters.

Based on the results of the performed experimental studies and the data presented in scientific publications (Figueiredo et al., 2017; Hossain et al., 2011; Khanmohammadi et al., 2015; M. Li et al., 2018; Yang et al., 2018), it would be practical and effective to carry out further studies only with biochar made at 600 °C and

analyze furthermore the effect of different initial pH value i.e., 7.5.

## Conclusion

1. Experimental studies have shown that the sludge ashes pyrolysis temperature has a significant effect on the phosphate adsorption efficiency. Maximum adsorption efficiency was recorded when the biochar was prepared at 600 °C.
2. It was observed that the highest values of equilibrium adsorption capacity (efficiency) were recorded for biochar prepared at 600 °C (at 100 mg/l initial solution  $q_e = 6$  mg/g, at 50 mg/l solution  $q_e = 2.6$  mg/g). The lowest efficiency was recorded for dry sludge granules (at 100 mg/l initial solution  $q_e = 1$  mg/g, at 50 mg/l solution  $q_e = 1.2$  mg/g) for both phosphate concentrations.
3. It was observed that the highest values of removal efficiency were recorded for biochar 600 °C (at 100 mg/l initial solution was 60 %, at 50 mg/l solution was 52 %), and the lowest efficiency was dry sludge granules (at 100 mg/l initial solution was 10 %, at 50 mg/l solution was 24 %) for both phosphate concentrations.
4. With an increase of pH in samples, higher values of equilibrium adsorption capacity and removal efficiency were recorded. Meanwhile, while comparing the different initial phosphate concentration pH values, it was found out that the higher the pH value the higher the sorption capacity values were.

## References

- Agrafioti, E., Bouras, G., Kalderis, D., & Diamadopoulos, E. (2013). Biochar production by sewage sludge pyrolysis. *Journal of Analytical and Applied Pyrolysis*, 101, 72–78. <https://doi.org/10.1016/J.JAAP.2013.02.010>
- Callegari, A., Hlavinek, P., & Capodaglio, A. G. (2018). Production of energy (biodiesel) and recovery of materials (biochar) from pyrolysis of urban waste sludge. *Revista Ambiente & Água*, 13(2). <https://doi.org/10.4136/AMBI-AGUA.2128>
- Chen, Y. di, Wang, R., Duan, X., Wang, S., Ren, N. qi, & Ho, S. H. (2020). Production, properties, and catalytic applications of sludge derived biochar for environmental remediation. *Water Research*, 187, 116390. <https://doi.org/10.1016/J.WATRES.2020.116390>
- Fang, L., Li, J. shan, Guo, M. Z., Cheeseman, C. R., Tsang, D. C. W., Donatello, S., & Poon, C. S. (2018). Phosphorus recovery and leaching of trace elements from incinerated sewage sludge ash (ISSA). *Chemosphere*, 193, 278–287. <https://doi.org/10.1016/J.CHEMOSPHERE.2017.11.023>
- Figueiredo, C., Lopes, H., Coser, T., Vale, A., Busato, J., Aguiar, N., Novotny, E., & Canellas, L. (2017). Influence of pyrolysis temperature on chemical and physical properties of biochar from sewage sludge. *Archives of Agronomy and Soil Science*, 64(6), 881–889. <https://doi.org/10.1080/03650340.2017.1407870>

- Gopinath, A., Divyapriya, G., Srivastava, V., Laiju, A. R., Nidheesh, P. v., & Kumar, M. S. (2021). Conversion of sewage sludge into biochar: A potential resource in water and wastewater treatment. *Environmental Research*, 194, 110656. <https://doi.org/10.1016/J.ENVRES.2020.110656>
- Hossain, M. K., Strezov Vladimir, V., Chan, K. Y., Ziolkowski, A., & Nelson, P. F. (2011). Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. *Journal of Environmental Management*, 92(1), 223–228. <https://doi.org/10.1016/J.JENVMAN.2010.09.008>
- Januševičius, T., Mažeikienė, A., Danila, V., & Paliulis, D. (2022). The characteristics of sewage sludge pellet biochar prepared using two different pyrolysis methods. *Biomass Conversion and Biorefinery*, 1, 1–10. <https://doi.org/10.1007/S13399-021-02295-Y/FIGURES/3>
- Karim, A. A., Kumar, M., Mohapatra, S., & Singh, S. K. (2019). Nutrient rich biomass and effluent sludge wastes co-utilization for production of biochar fertilizer through different thermal treatments. *Journal of Cleaner Production*, 228, 570–579. <https://doi.org/10.1016/J.JCLEPRO.2019.04.330>
- Khanmohammadi, Z., Afyuni, M., & Mosaddeghi, M. R. (2015). Effect of pyrolysis temperature on chemical and physical properties of sewage sludge biochar. *Waste Management and Research*, 33(3), 275–283. <https://doi.org/10.1177/0734242X14565210>
- Li, J., Li, B., Huang, H., Lv, X., Zhao, N., Guo, G., & Zhang, D. (2019). Removal of phosphate from aqueous solution by dolomite-modified biochar derived from urban dewatered sewage sludge. *Science of The Total Environment*, 687, 460–469. <https://doi.org/10.1016/J.SCITOTENV.2019.05.400>
- Li, M., Tang, Y., Lu, X. Y., Zhang, Z., & Cao, Y. (2018). Phosphorus speciation in sewage sludge and the sludge-derived biochar by a combination of experimental methods and theoretical simulation. *Water Research*, 140, 90–99. <https://doi.org/10.1016/J.WATRES.2018.04.039>
- Lietuvos Respublikos aplinkos ministerija. (2006). *Dėl Nuotekų tvarkymo reglamento patvirtinimo* (2006, gegužės 17, Nr. D1-236). <https://e-seimas.lrs.lt/portal/legalAct/lt/TAD/TAIS.276576/asr>
- Lietuvos socialinių mokslų centro Ekonomikos ir kaimo vystymo institutas. (2020). *Žvilgsnis į žiedinę ekonomiką. Nuotekų dumblo tvarkymo gerosios praktikos*. [https://www.laei.lt/files\\_static/NUOTEKU\\_DUMBLO\\_TVARKYMO\\_GEROSIOS\\_PRAKTIKOS.pdf](https://www.laei.lt/files_static/NUOTEKU_DUMBLO_TVARKYMO_GEROSIOS_PRAKTIKOS.pdf)
- Liu, H., Hu, G., Basar, I. A., Li, J., Lyczko, N., Nzihou, A., & Eskicioglu, C. (2021). Phosphorus recovery from municipal sludge-derived ash and hydrochar through wet-chemical technology: A review towards sustainable waste management. *Chemical Engineering Journal*, 417, 129300. <https://doi.org/10.1016/J.CEJ.2021.129300>
- Lu, H., Zhang, W., Wang, S., Zhuang, L., Yang, Y., & Qiu, R. (2013). Characterization of sewage sludge-derived biochars from different feedstocks and pyrolysis temperatures. *Journal of Analytical and Applied Pyrolysis*, 102, 137–143. <https://doi.org/10.1016/J.JAAP.2013.03.004>
- Ma, Y., Li, P., Yang, L., Wu, L., He, L., Gao, F., Qi, X., & Zhang, Z. (2020). Iron/zinc and phosphoric acid modified sludge biochar as an efficient adsorbent for fluoroquinolones antibiotics removal. *Ecotoxicology and Environmental Safety*, 196, 110550. <https://doi.org/10.1016/J.ECOENV.2020.110550>
- Nobaharan, K., Novair, S. B., Lajayer, B. A., & Hullebusch, E. D. van. (2021). Phosphorus removal from wastewater: the potential use of biochar and the key controlling factors. *Water* 2021, 13(4), 517. <https://doi.org/10.3390/W13040517>
- Sincero, A. P.; Sincero, G. A. (2003). *Physical-chemical treatment of water and wastewater*. IWA Publishing.
- Singh, S., Kumar, V., Dhanjal, D. S., Datta, S., Bhatia, D., Dhiman, J., Samuel, J., Prasad, R., & Singh, J. (2020). A sustainable paradigm of sewage sludge biochar: valorization, opportunities, challenges and future prospects. *Journal of Cleaner Production*, 269, 122259. <https://doi.org/10.1016/J.JCLEPRO.2020.122259>
- Wang, H., Xiao, K., Yang, J., Yu, Z., Yu, W., Xu, Q., Wu, Q., Liang, S., Hu, J., Hou, H., & Liu, B. (2020). Phosphorus recovery from the liquid phase of anaerobic digestate using biochar derived from iron-rich sludge: A potential phosphorus fertilizer. *Water Research*, 174, 115629. <https://doi.org/10.1016/J.WATRES.2020.115629>
- Wang, Z., Miao, R., Ning, P., He, L., & Guan, Q. (2021). From wastes to functions: A paper mill sludge-based calcium-containing porous biochar adsorbent for phosphorus removal. *Journal of Colloid and Interface Science*, 593, 434–446. <https://doi.org/10.1016/J.JCIS.2021.02.118>
- Yang, Q., Wang, X., Luo, W., Sun, J., Xu, Q., Chen, F., Zhao, J., Wang, S., Yao, F., Wang, D., Li, X., & Zeng, G. (2018). Effectiveness and mechanisms of phosphate adsorption on iron-modified biochars derived from waste activated sludge. *Bioresource Technology*, 247, 537–544. <https://doi.org/10.1016/J.BIORTECH.2017.09.136>
- Yin, Q., Liu, M., & Ren, H. (2019). Biochar produced from the co-pyrolysis of sewage sludge and walnut shell for ammonium and phosphate adsorption from water. *Journal of Environmental Management*, 249, 109410. <https://doi.org/10.1016/J.JENVMAN.2019.109410>

## NUOTEKŲ DUMBLO PELENŲ NAUDOJIMAS FOSFATAMS IŠ NUOTEKŲ VALYTI

J. Paulionytė, R. Vaiškūnaitė, A. Mažeikienė

Santrauka

Fosforas yra svarbus aplinkoje, todėl būtinas jo atgavimas ir perdirbimas. Nuotekos yra viena iš vietų, kur randamas didelis fosforo ir jo junginių kiekis. Dėl to vandenyje esantis fosforas yra viena iš aplinkos problemų, tokių kaip eutrofikacija. Didelis nuotekų dumblo kiekis ir jo naudojimas yra viena iš problemų, su kuria susiduriama tiek dideliuose miestuose, tiek mažesniuose miesteliuose. Šiuo tyrimu siekiama nustatyti, kiek ir kaip naudoti nuotekų dumblo pelenus kaip bioanglį, siekiant fosforo junginius pašalinti iš nuotekų. Galiausiai šiame straipsnyje pabrėžiamas bioanglies sorbcijos gebėjimas absorbuoti fosforo junginius, kurie buvo apskaičiuoti ir palyginti su kitų tyrėjų gautais rezultatais.

**Reikšminiai žodžiai:** bioanglis, dumblo pelenai, fosfatas, adsorbicija, nuotekos, nuotekų dumblas, fosfato valymas, fosforas.