INNOVATIVE SOLUTIONS FOR PHOSPHORUS REMOVAL IN MUNICIPAL WASTEWATER: PRIMARY AND POST-TREATMENT APPROACHES

Dagnija Grabuza[1], Linda Grinberga[1], Ruta Ozola-Davidane[1], Julija Karasa[1, 2]
[1]Latvia University of Life Sciences and Technologies, Latvia; [2]University of Latvia, Latvia
dagnija.grabuza@lbtu.lv , linda.grinberga@lbtu.lv, ruta.ozola-davidane@lbtu.lv, julija.karasa@lu.lv

Abstract. Excess phosphorus (P) in wastewater contributes to eutrophication, highlighting the need for efficient removal technologies across both decentralized and centralized wastewater treatment systems. This study evaluates two filtration-based approaches utilizing mineral-based sorbents for enhanced P removal. In decentralized settings, a prototype system integrating lightweight expanded clay aggregate (LECA) was tested for primary treatment of domestic wastewater. In parallel, Polonite®, a calcium-rich sorbent, was applied as a post-treatment solution for municipal effluents in centralized facilities. Both systems were implemented and monitored under real-world operational conditions in Latvia. LECA demonstrated limited and inconsistent P removal efficiency (9-27%), indicating insufficient performance as a standalone filter. While Polonite® achieved consistent removal efficiencies ranging from 63% to 99%, with final effluent concentrations consistently below Latvia's regulatory limit of $2\ \mathrm{mg\ P \cdot L^{-1}}$. Scanning electron microscopy analysis revealed morphological changes on Polonite® surfaces after filtration, confirming adsorption and precipitation of P-containing compounds. The findings highlight Polonite® as an effective and reliable material for post-treatment polishing in centralized wastewater systems, while LECA may serve only as a preliminary filter in decentralized applications.

Keywords: phosphorus removal, adsorption, wastewater treatment, prototype, mineral-based sorbents.

Introduction

Excess phosphorus (P) in wastewater contributes to eutrophication, posing a significant environmental challenge for decentralized and municipal treatment systems. Conventional methods such as chemical precipitation using aluminium, iron, or calcium-based coagulants remain effective, particularly in treating high P influents, yet may pose challenges in decentralized systems due to chemical supply requirements and operational complexity [1-3]. In contrast, biological approaches such as Enhanced Biological Phosphorus Removal (EBPR) offer low-cost, sustainable alternatives suitable for smaller systems, with research also supporting the use of plants and microalgae to enhance nutrient uptake [4-6].

While conventional and biological methods focus on P removal, integrated solutions such as struvite crystallization go a step further by enabling nutrient recovery and reuse. Through this process, P is transformed into struvite – a slow-release fertilizer with high value for agricultural applications [7; 8].

Among recent developments, adsorption techniques using mineral-based sorbents - such as natural and modified zeolites, clays, and calcium-rich materials - have gained attention as effective, low-cost options for P removal. These sorbents, often modified with lanthanum or zirconium, can achieve high adsorption capacities, in some cases exceeding $100\ \mathrm{mg\ P \cdot g^{-1}}$, through mechanisms like ligand exchange, precipitation, and inner-sphere complexation [9-12]. Their high removal efficiencies, regeneration potential, and material availability make them promising materials for sustainable P management in both centralized and decentralized systems [10-13].

This study aims to evaluate the effectiveness of two filtration-based solutions using mineral-based materials for enhancing P removal in wastewater treatment systems (WWTS). The first approach targets decentralized systems, employing a prototype that integrates lightweight expanded clay aggregates (LECA) to enhance P removal during the initial treatment phase. In contrast, the second solution is tailored for centralized WWTS, employing Polonite® as a post-treatment filter to eliminate residual P before final discharge. Both prototypes were implemented and monitored under real-world operational conditions to assess their P removal efficiency, material performance, and potential for broader application.

Materials and methods

As part of this study, a prototype biological wastewater treatment unit incorporating an advanced P removal function was designed and experimentally evaluated for the treatment of domestic wastewater from a single-family home. The prototype design adhered to the regulatory framework currently in force in Latvia, with system parameters specifically adapted to the operational requirements of decentralized

DOI: 10.22616/ERDev.2025.24.TF210

household WWTS. The experimental investigation was conducted under real-world conditions in the city of Jelgava, where a controlled monitoring system regulated wastewater inflow, maintaining a constant flow rate of 0.9 $m^3 \cdot day^{-1}$ with the pump activation occurring 3 times per day. To quantify P removal efficiency, influent and effluent samples were collected and subjected to laboratory analysis, with phosphate-phosphorus (PO_4-P) and total phosphorus (P_{tot}) concentrations measured at distinct treatment stages. The treatment system comprised a filtration unit utilizing LECA as a filtering medium (particle size fraction d10–14 mm) in combination with an aeration module operating with activated sludge (Fig. 1A). Monitoring data were systematically collected and analysed to assess the prototype's efficacy in P reduction and to determine its overall suitability for integration into decentralized household wastewater treatment applications.

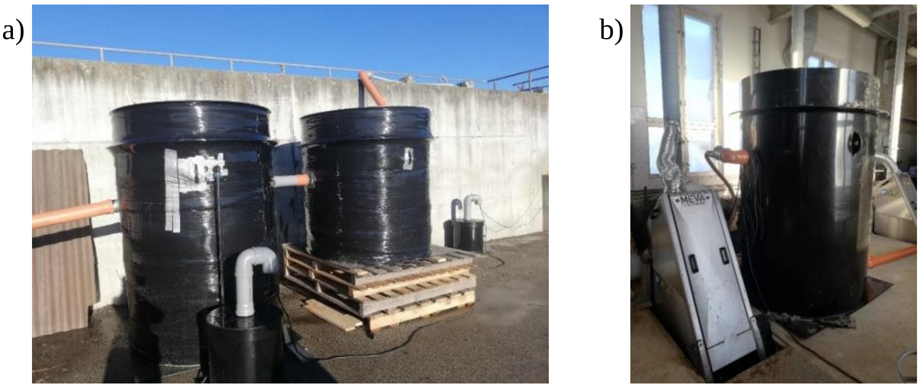


Fig. 1. **Prototype biological wastewater treatment unit with LECA (A) and with Polonite® (B)**

A filter medium, Polonite®, sourced from Ecofiltration, was integrated into the prototype as a post-treatment unit (Fig. 1B). Polonite® was selected for its high P adsorption efficiency, reported to range from 59% to 95% [14]. Following biological treatment, wastewater entered a sedimentation chamber to remove excess sludge before passing through the Polonite® filtration chamber. The opoka-based Polonite® material has a high surface area and selective chemical adsorption, immobilizing P while allowing other components to pass. P remained chemically stabilized, preventing release back into the environment [14]. The prototype was installed at the Limbažu siltums LTD wastewater treatment facility in Limbaži (Latvia) receiving municipal wastewater. Performance monitoring involved cumulative flow measurements and P concentration analysis. Polonite® filters were designed for 2-4 years of operation, after which the spent material could be repurposed as a phosphorus-rich soil amendment for agriculture.

To evaluate the phosphorus removal efficiency of the treatment system, water samples were collected and analysed for P_{tot} concentrations at three designated control points. The inflow sampling point represents untreated wastewater prior to entering the treatment units. The midpoint sampling point corresponded to the effluent after passing through the prototype filtration unit containing expanded clay aggregate, but before entering the industrial biological treatment system. The outflow sampling point was located at the discharge point following treatment in the industrial biological unit. Water sampling was conducted twice per month, with P_{tot} concentrations analysed to assess removal efficiency at each stage.Additionally, the filter medium Polonite® was used to scale up the laboratory prototype (approximately 25 times) for post-treatment of municipal wastewater effluents. The cylindrical filter unit filled with Polonite® was experimentally evaluated under real-world conditions at the Ādaži wastewater treatment plant (PE 23,066), where a controlled flow rate of 120 $L \cdot h^{-1}$ was maintained. For phosphorus removal simulation, 1 m^3 of pre-treated effluent with an initial P concentration of 2.3 $mg \cdot L^{-1}$ was used. The prototype's performance was assessed by hourly measurements of PO_4-P concentrations in the effluent after filtration.

Composition of the mineral-based materials were determined by the X-ray Powder diffraction analysis (PXRD) performed on Bruker D8 Advance powder diffractometer equipped with LynxEye position-sensitive detector and Cu Kα radiation ($\lambda = 1.54060$ Å), 40 kV, 40 mA. The diffraction patterns were recorded with 0.02 step size and a scan speed of 0.5 s per step in the 2θ range from 5 to 50. The chemical composition of materials was determined by wavelength dispersive X-ray fluorescence (WDXRF) spectrometer Bruker S8 TIGER. Air-dried samples were crushed into fine powder and pressed into pellets (diameter – 8 mm) and analysed in Vacuum mode. The analyses were performed in the Best detection mode, displaying measurement results in oxide formula units. The scanning electron microscopy (SEM) data were obtained to evaluate the morphology of the samples using the scanning electron microscope FE-SEM Hitachi S4800 (Tokyo, Japan). The samples were measured in the secondary electron regime, with the SEM operating voltage being 3–5 kV.

Quantification of remaining phosphorus (as P_{tot}, $mg \cdot L^{-1}$) in wastewater samples was performed on the spectrophotometer Hach 3900 coupled with the thermostat HT200S (Hach-Lange, Germany) by molybdovanadate method with acid persulfate digestion LCK 348 (for PO_4-P range 0.5-5.0 $mg \cdot L^{-1}$). Before the analysis, samples were filtered through 0.45 μm syringe filters and diluted if necessary. The P_{tot} concentration in wastewater samples was determined using the method specified in LVS EN ISO 6878:2005, Section 7, with a detection limit of 0.10 $mg \cdot L^{-1}$.

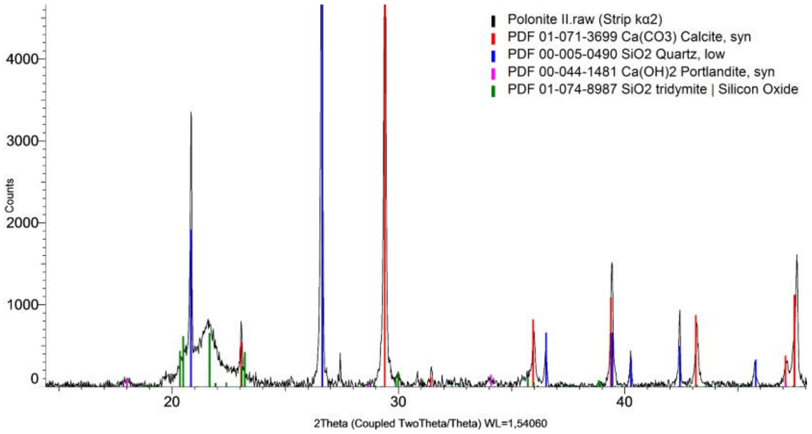
Phosphorus removal efficiency (%) was calculated using the following equation:

$$\text{Removal\%} = \frac{C_0 - C_e}{C_0} \times 100, \tag{1}$$

where C_0 – initial concentration of P in the solution ($mg \cdot L^{-1}$);
C_e – final concentration of P in the solution ($mg \cdot L^{-1}$).

Results and discussion

Polonite® is derived from thermally heated mineral opoka rock in accordance with PXRD data consisting mostly of SiO_2 and $CaCO_3$ (Fig. 2), whereas the main elements characterising the chemical composition of Polonite® are silicon, calcium, aluminium, iron and oxygen. While LECA chemical composition includes: SiO_2, Al_2O_3, Fe_2O_3, CaO and some alkalis such as Na_2O and K_2O [15].



Compound	**Content, %**
SiO_2	64.95
CaO	23.23
Al_2O_3	7.60
Fe_2O_3	2.43
K_2O	1.16
TiO_2	0.34
SO_3	0.16

Fig. 2. **PXRD pattern and chemical composition of Polonite®**

The initial Polonite® has a porous, irregular surface with distinct granules and visible cavities that could promote P adsorption and surface interactions (Fig. 3A). After P adsorption, the surface appeared more compact and covered with fine particulates, indicating deposition and possible precipitation of P-containing compounds (Fig. 3B).

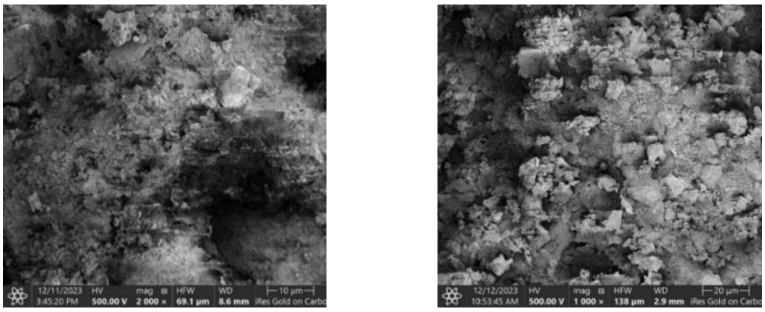


Fig. 3. **SEM images (1 k and 2 k magnification) of initial Polonite® (A) and Polonite® after P removal using a centralized system prototype in Ādaži WWTP (B)**

This morphological change supports the interaction between Polonite® and P, aligning with the observed 75% reduction in P concentration (from 2.3 to 0.57 mg·L^{-1}) during filtration.

The efficiency of Polonite® in removing residual P from municipal wastewater effluents was monitored over a 5-hour period during the operation of the centralized treatment prototype (Fig. 4). The initial PO_4-P concentration in the influent was approximately 2.3 mg P·L^{-1}. Polonite® exhibited significantly high P removal efficiency at the start of the experiment, achieving a maximum of 99% removal at 0 h, which reflects the immediate adsorption and chemical interaction capacity high at 98% after 2 hours, indicating the media’s strong early performance stability.

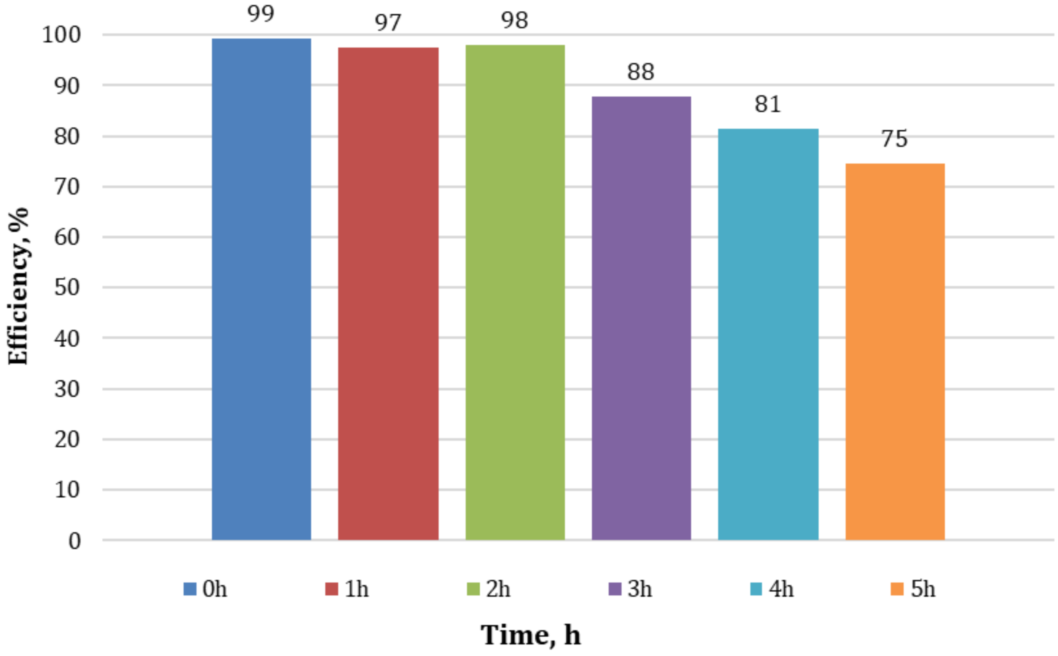


Fig. 4. **Efficiency of Polonite® to remove the remaining P from Ādažu WWTP (initial PO_4-P ~2.3 mg P·L^{-1})**

As the operational time progressed, a gradual decline in P removal efficiency was observed – 88% at 3 h, 81% at 4 h, and 75% at 5 h respectively (Fig. 4). This trend suggests progressive saturation of the active sites and possible clogging or coating of the media surface with reaction products, as also visually supported by SEM images (Fig. 4). Despite this decline, the Polonite® filter consistently maintained P concentrations below the 2 mg P·L^{-1} regulatory threshold set for effluent discharge in Latvia, confirming its suitability for real-world applications in centralized systems.

The P removal performance using LECA in a decentralized treatment setup showed limited and inconsistent efficiency over the monitoring period (Fig. 5A). The P_{tot} concentrations in the “Middle” stage (post-LECA, pre-biological treatment) were only slightly lower than inflow values, while final outflow values after the full treatment process showed modest reductions. P removal efficiency ranged from 9% to 27%, with significant fluctuations between sampling dates. This suggests that LECA alone, despite its porous structure, is insufficient for effective P removal when used as a primary filtration medium. In contrast, the centralized post-treatment unit in Limbaži WWTP using Polonite® demonstrated consistently high P removal efficiency, with final effluent concentrations mainly below 1 mg P·L^{-1} (Fig. 5B). Removal efficiencies ranged from 63% to 86%, maintaining performance across all sampling dates.

The P removal performance using LECA in a decentralized treatment setup showed limited and inconsistent efficiency over the monitoring period (Fig. 5). The P_{tot} concentrations in the “Middle” stage (post-LECA, pre-biological treatment) were only slightly lower than inflow values, while final outflow values after the full treatment process showed modest reductions. P removal efficiency ranged from 9% to 27%, with significant fluctuations between sampling dates. This suggests that LECA alone, despite its porous structure, is insufficient for effective P removal when used as a primary filtration medium.

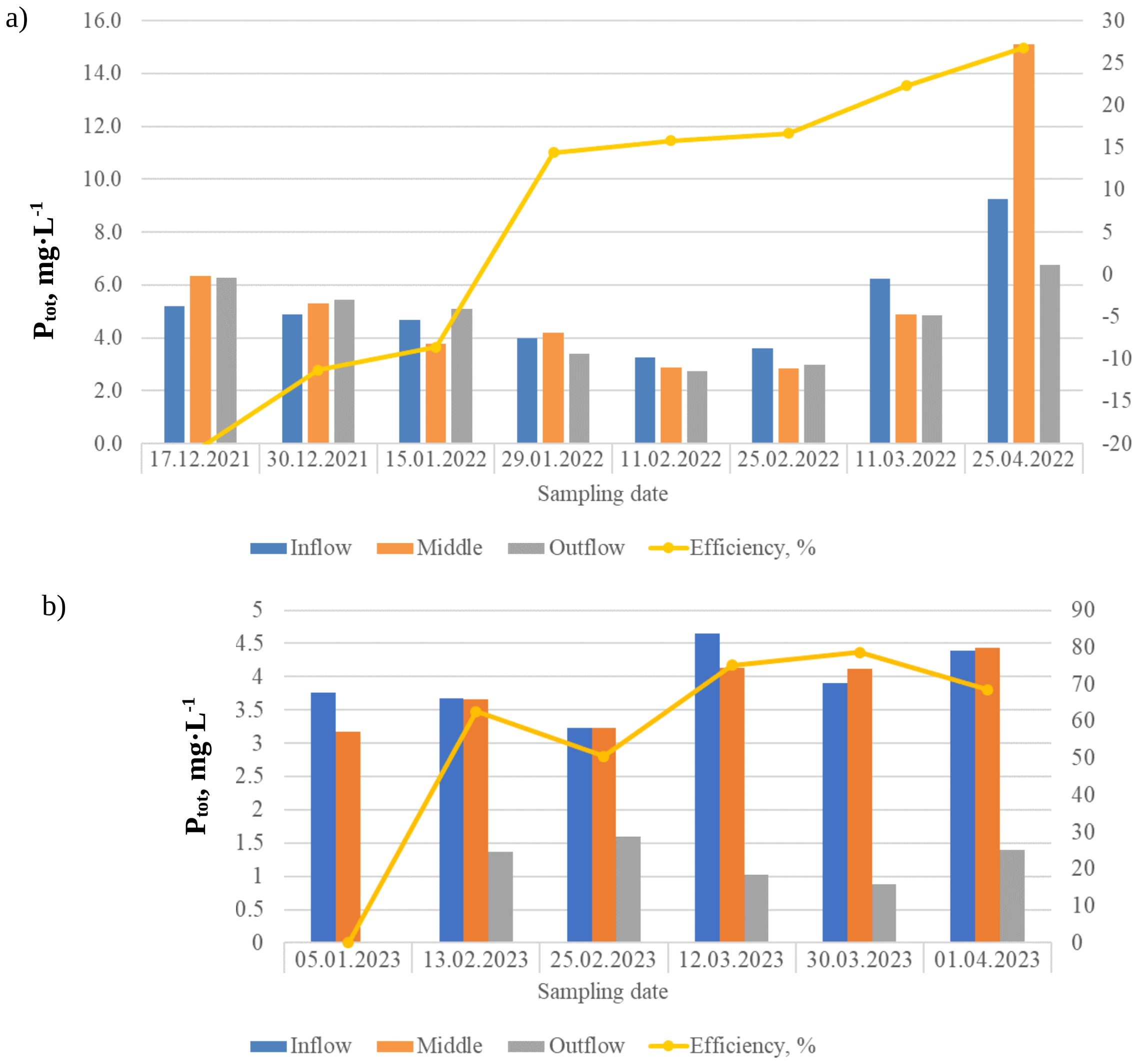


Fig. 5. **Total phosphorus efficiency with LECA (A) and with Polonite® (B)**

In contrast, the centralized post-treatment unit using Polonite® demonstrated consistently high P removal efficiency, with final effluent concentrations frequently below 1 mg P·L^{-1}. Removal efficiencies ranged from 63% to 86%, maintaining performance across all sampling dates. This highlights Polonite®'s strong adsorption capacity and its suitability for polishing treatment in municipal settings.

These results emphasize the importance of selecting appropriate filter materials based on the scale and stage of the treatment. While LECA may provide some preliminary benefit in decentralized systems, Polonite® clearly outperforms it in both consistency and overall effectiveness, especially for post-treatment polishing centralized facilities.

Conclusions

1. LECA filtration in decentralized systems demonstrated limited and inconsistent phosphorus removal efficiency, with performance ranging between 9% and 27%. These results indicate that LECA, when used alone, is not sufficient for reliable P removal in small-scale wastewater treatment applications.
2. Polonite® post-treatment in centralized systems showed consistently high P removal efficiency, ranging from 63% to 99%. Effluent P concentrations remained below the regulatory limit of 2 mg P·L^{-1}, confirming Polonite® as an effective polishing step for municipal wastewater treatment.
3. Material surface analysis using SEM revealed morphological changes in Polonite® after filtration, including surface compaction and particle deposition, indicating successful adsorption and potential precipitation of P compounds.

4. Comparative evaluation underscores the importance of selecting appropriate filter media based on the system scale and treatment stage. While LECA may provide marginal benefit in preliminary filtration, Polonite® is better suited for consistent and effective post-treatment phosphorus removal.

Acknowledgements

Administration of Latvian Environmental Protection Fund projects No. 1-08/86/2024 “Innovative solution for wastewater treatment and phosphorus recovery” and No.1-08/92/2023 “Evaluation of the application of filter L for the recovery of phosphorus from wastewater for the promotion of circular economy”. The Investment and Development Agency of Latvia financed Voucher project “Biological Treatment Facilities with Enhanced Total Phosphorus Removal”.

Author contributions

Conceptualization, D.G., R.O.D., methodology, L.G and J.K; formal analysis, L.G, R.O.D, D.G. and J.K; investigation, J.K., L.G. and D.G., writing – original draft preparation, L.G., R.O.D; writing – review and editing, D.G., J.K. and R.O.D., visualization, L.G., R.O.D., J.K. All authors have read and agreed to the published version of the manuscript.

References

[1] Lei C., Liu B., Liu Y., Li Y. Design a project of sewage plant to make the cross-section water quality reach standard. E3s Web of Conferences, 252, 2021, 03038. DOI: 10.1051/e3sconf/202125203038

[2] Roni N., Adnan S., Hamidon N., Ismail T. An overview of the removal phosphorus in wastewater. Journal of Advanced Industrial Technology and Application, 1(2). 2020. DOI: 10.30880/jaita.2020.01.02.001

[3] Ai H. N., Li M. L., He Q. Simulation and optimization of denitrifying phosphorus removal in A2/O. Advanced Materials Research, 374, 2012, pp. 553-559. DOI: 10.4028/www.scientific.net/AMR.374-377.553

[4] He Z. Effect of granular matrix on functional flora in ebpr system. Iop Conference Series Earth and Environmental Science, 1035(1), 2022, 012003. DOI: 10.1088/1755-1315/1035/1/012003

[5] Zeng R., Lemaire R., Yuan Z., Keller J. Simultaneous nitrification, denitrification, and phosphorus removal in a lab-scale sequencing batch reactor. Biotechnology and Bioengineering, 84(2), 2003, pp. 170-178. DOI: 10.1002/bit.10744

[6] Mažeikienė A. and Šarko J. Additional treatment of nitrogen and phosphorus using natural materials in small-scale domestic wastewater treatment unit. Water, 15(14), 2023, 2607. DOI: 10.3390/w15142607

[7] Li Q., Wang S., Wang L., Zhang L., Wan X., Sun Z. The recovery of phosphorus from acidic ultra-high phosphorous wastewater by the struvite crystallization. Water, 12(4), 2020, 946. DOI: 10.3390/w12040946

[8] Desmidt E., Ghyselbrecht K., Zhang Y., Pinoy L., Bruggen B., Verstraete W., … & Meesschaert B. Global phosphorus scarcity and full-scale p-recovery techniques: a review. Critical Reviews in Environmental Science and Technology, 45(4), 2014, pp. 336-384. DOI: 10.1080/10643389.2013.866531

[9] Xie J., Wang Z., Fang D., Li C., Wu D. Green synthesis of a novel hybrid sorbent of zeolite/lanthanum hydroxide and its application in the removal and recovery of phosphate from water. J. Colloid Interface Sci. 2014, 423, pp. 13-19. DOI: 10.1016/j.jcis.2014.02.020.

[10] Kong L., Tian Y., Li N., Liu Y., Zhang J., Zhang J., Zuo W. Highly-effective phosphate removal from aqueous solutions by calcined nano-porous palygorskite matrix with embedded lanthanum hydroxide. Appl. Clay Sci., 2018, 162, pp. 507-517. DOI: 10.1016/j.clay.2018.07.005

[11] Shi W., Fu Y., Jiang W., Ye Y., Kang J., Liu D., Ren Y., Li D., Luo C., Xu Z. Enhanced phosphate removal by zeolite loaded with Mg-Al-La ternary (hydr)oxides from aqueous solutions: Performance and mechanism. Chem. Eng. J. 2019, 357, pp. 33-44. DOI: 10.1016/j.cej.2018.08.003

[12] Luo Q., Wei J., Guo Z., Song Y. Adsorption and immobilization of phosphorus from water and sediments using a lanthanum-modified natural zeolite: Performance, mechanism and effect. Sep. Purif. Technol., 2024, 329, 125187. DOI: 10.1016/j.seppur.2023.125187

[13] Zeng G., Li G., Wu Y., Tang C., Yuan W., Zhong H., Deng N., Liu Q., Liu J., Ouyang K., Hu X., Yang X. Preparation of high specific surface area Zn/Al/Zr LDH@HTCC for enrichment and recovery of phosphorus from water. Surf. Interfaces, 2023, 42, 103330. DOI: 10.1016/j.surfin.2023.103330

[14] Gubernat S., Masłoń A., Czarnota J., Koszelnik P. Phosphorus removal from wastewater using marl and travertine and their thermal modifications. Desalination and Water Treatment, 275, 2022, pp. 35-46. DOI: 10.5004/dwt.2022.28529

[15] Uysal O., Uslu İ., Aktaş C.B., Chang B., Yaman İ.Ö. Physical and Mechanical Properties of Lightweight Expanded Clay Aggregate Concrete. Buildings 2024, 14, 1871. DOI: 10.3390/buildings14061871