

Review of Phosphate Removal From Water by Various Sorbents

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Abstract

Phosphate is a major pollutant that deteriorates water quality. Adsorption technology is amongst the different technologies used to decrease the phosphate levels in water, and has been found to be highly effective even at low phosphate concentrations. La modified bio-ceramisite (La@BC) is a recyclable granular adsorbent. A layered zinc hydroxide (LZH) was synthesized by a simple precipitation method and Industrial by-products (bottom ash (BA)) has gained increasing attentions because of their intriguing characteristic for phosphate removal. Considering the importance of the topic, this study reviews the reported literature in the field of adsorptive removal of phosphate over various adsorbents such as Lanthanum (La)-based adsorbents, bottom ash And Layered zinc hydroxide. Moreover, insights into the adsorption behavior, experimental parameters, mechanisms, and the possible desorption processes of phosphate onto Lanthanum (La)-based adsorbents, bottom ash and Layered zinc hydroxide are also considered. Finally, research challenges and gaps have been highlighted. Based on this review, future research about phosphate removal is also discussed & reviewed.

Introduction

Lanthanum (La), a chemically stable and environmentally friendly rare metal. It has gained considerable attentions because La^{3+} has a strong affinity toward phosphate. La can combined with PO_3 stable and sparingly soluble precipitation ($LaPO_4$) [Koilraj, and Sasaki (2017)]. Recently many La based adsorbents such as La modified bentonite [Lucena-Silva et al. (2019), Slaný et ai. (2019)], zeolite [Shi et al. (2019)], activated carbon fiber [Xia et al.(2021)], mesoporous silica [Chen et al.(2019)] have been used for phosphate removal from wastewater and eutrophication control in water ecosystem. Compared with Al and Fe elements, La based adsorbent has a higher phosphate removal efficiency under diverse environmental conditions [Chen et al.(2020) , Dong et al.(2017)]. It has hardly pose an adverse effect for ecological organisms as well as humans [D'Haese et al. (2019)]. Layered metal hydroxides are an important family of layered sheet-like materials that include layered single metal hydroxides (LSHs) and layered double hydroxides (LDHs) which comprise a dual metal cations in the host layer. LMHs are characterized by having a structure similar to the natural mineral brucite, consisting of metal hydroxyl layers and interlayer charge balancing anions. Over the past decade, LMHs have gained reputable success in terms of their convenient synthesis, structure, and modification. [Yin and Tang (2016)] Their ease of tailoring has enabled them to meet the requirements of practical applications in various fields such as catalysis, energy conversion and storage, magnetism, thin film gadgets, adsorption/ion exchange materials, and additives in fire-retardants. [Yin and Tang (2016), Rogez et al. (2011)] Layered zinc hydroxides (LZHs) fall into the category of LSHs, and typically carry the formula of $Zn_5(OH)_8(A)_2nH_2O$, where A is an intercalated anion (i.e. carbonate, hydroxyl, nitrate, carboxylate, sulfate). [Leung et al. (2018)]. The general layered structure is based on zinc hydroxide layers comprising



octahedrally and tetrahedrally coordinated zinc ions.[Gordeeva et al.(2020)] The inter-layer anions act as exchangeable anions that neutralize the positive charge of the zinc hydroxide laminates, hence, they provide LZHs with high anion-exchange capacity.[Gordeeva et al.(2020), Tran et al.(2018)] The appealing feature of LZHs is their easy synthesis, high anion-exchange capacity relative to LDH, and the ability of mixing Zn with other metals to convert LZH to an LDH salt. [Demel et al.(2011)]. Bottom Ash (BA), mainly consists of inorganic and non-combustible particles that remain in the bottom of the combustion chamber due to their relatively heavy weight and large size (Kirk et al. 2003). Although BA is rich in iron and aluminium oxides, the majority of BA is wasted in landfills (Hjelmar et al. 2010) that requires expensive land and transportation investments. However, due to the attractive chemical composition and free availability of BA, some trials have been made to recycle it in some applications, such as the concrete industry (Zhang & Poon 2015; Shubbar et al. 2018). However, fresh BA from power plants has not been used in water treatment yet. Few trials were made to use nano- powder of BA in water treatment (Alwash 2017), which have limited applications due to the high production cost (production of nanopowder) and the safety concerns (Tyagi et al. 2018). In the present study, the BA has been utilised as an economically efficient adsorbent for phosphate. The selection of the BA here is due to two main reasons: firstly, because the BA is rich in iron aluminium oxides (as stated in the results section of this study), that gives it a good potential capacity for phosphate sorption. Secondly, the BA itself is classified as an industrial by-product that is environmentally harmful and it usually requires expensive management plans (Jamaludin et al. 2019). Thus, utilizing this by-product in water treatment is environmentally and economically beneficial. There are different research where discuss about phosphate removal mechanisms using different adsorbent. In this study, I review various phosphate based adsorbent. On the review various phosphate removal mechanisms using different adsorbent will be known & it will expedite further scope of research.

2. Materials & Methods:

2.1. Materials

Biochar is generated from sewage sludge pyrolysis process. Zinc acetate ($Zn(OAc)_2$) and sodium hydroxide (NaOH).

2.2. Synthesis of La-modified granular adsorbent (La@BC)

(1) Preparation of granular bio-ceramisite (BC) :

Primarily biochar and fly ash (100 g, mass ratio of 2:8) were mixed. Then it was granulated into roughly spherical pellets with diameters of 8–12 mm by adding 80 mL distilled water. These pellets were then dried at 105 °C in an oven until they reached constant weight. Then dried pellets were firing in a laboratory-scale electric furnace at 1100 °C for 30 min. Finally, BCs were produced.

(2) Synthesis of La@BC: La@BCs were synthesised by co-precipitation method. 5.347 g $LaCl_3 \cdot 7H_2O$ (analytical grade, AG) dissolved with 100 mL distilled water in a 200 mL beaker. Then the Solutions containing 2 wt% of La were prepared. Firstly, BCs (100 g) were soaked in $LaCl_3$ solution for 4 h under a constant stirring of 120 rpm. A solution with 0.1 mol/L NaOH



was then slowly poured into the above baker to adjust pH value to 10. After stirring for 2 h, La(OH)₃ modified products were washed by distilled water until no Cl⁻ leaching (AgNO₃ titration method) and then dried in an oven at 60 °C for 4 h. Finally, La@BC adsorbents were obtained after heated at 300 °C for 30 min in an electric furnace.

2.3. Synthesis of LZH

Layered zinc hydroxides (LZHs) were prepared from zinc acetate via precipitation process requiring only two chemicals, zinc acetate and NaOH. Zinc acetate (20 g) was dissolved in 600 mL of deionized water. Approximately 5 g of NaOH was dissolved in 100 mL deionized water. The NaOH solution was added drop- wise to the zinc acetate solution until the pH reached 7 (0.2) or until the pH was stable and was unaffected after the addition of the base. The mixing was carried out at 45 °C at a rate of 400 rpm for 24 h. The resulting slurry was filtered in a 0.45 mm mixed cellulose filter (Whatman), washed with deionized water and dried at 90.

2.4. Batch experiments

All chemicals reagent used in this experiment were of analytical grade. Phosphate stock solutions with 1 g P/L were prepared by KH₂PO₄ and distilled water. In all adsorption experiments, working solutions with different initial phosphate concentrations were prepared by suitable dilution of the phosphate stock solution. Solutions with 0.1 mol/L HCl or 0.1 mol/L NaOH were used to adjust the initial pH values of working solutions. The residual phosphate concentrations were determined by the ammonium molybdate spectrometric method. All the batch experiments were performed in triplicates. To evaluate the reusability of La@BC on phosphate removal, batch adsorption-desorption experiments were conducted over five consecutive cycles. As desorption performance of adsorbent is strongly dependent on pH, 1 mol/L NaOH solution was used as a regenerant. Fig-1 shows the phosphate removal by Batch process using La@BC adsorbents, Fig-2 shows the phosphate removal by Batch process using LZH adsorbents & Fig-3 shows the phosphate removal by Batch process using BA adsorbents.



Fig-1: Flow chart about phosphate removal by Batch process using La@BC adsorbents



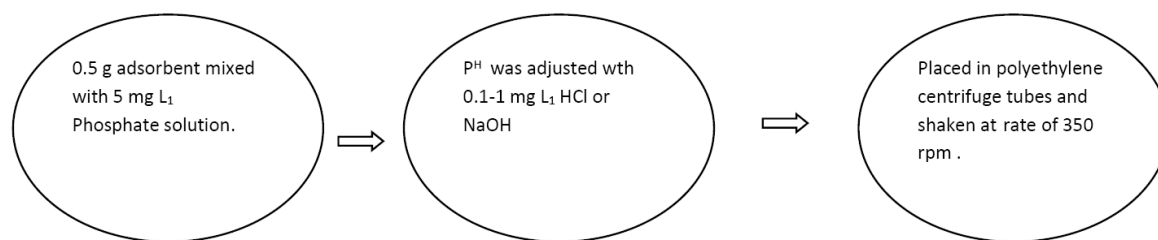


Fig-2: Flow chart about phosphate removal by Batch process using LZH adsorbents

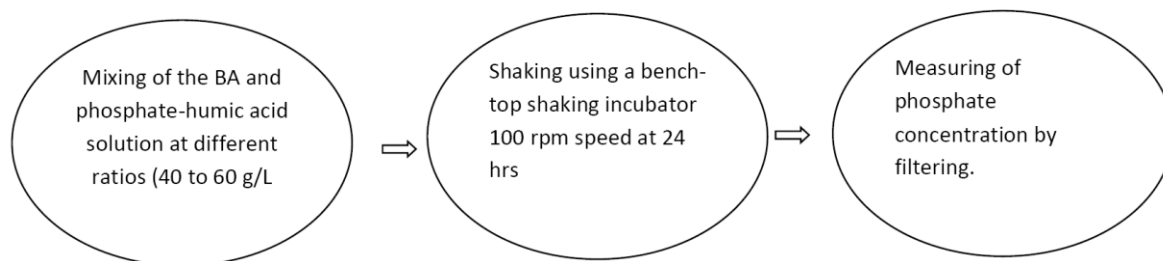


Fig-3: Flow chart about phosphate removal by Batch process using BA adsorbents.

The effect of contact time, solution pH, initial phosphate concentration, and co-existing ions were examined. All experiments were conducted in duplicates and at room temperature. LZH dosage experiments were conducted at different adsorbent amounts ranging between 0.5 and 200 g L⁻¹. The sorbent dose of 0.5 g L⁻¹ was found to be the most efficient and economic dose from preliminary experiments and was used for the subsequent experiments. All of the core level spectra were taken with a normal emission and a pass energy of 20 eV. The binding energy positions were calibrated with respect to the adventitious C–C signal at 284.8 eV. Zeta potential analysis of the LZH material was conducted on a Malvern Zetasizer Ultra equipment. The analysis of phosphate and other anions were conducted on a Dionex Ion optimum adsorption capacity. Experiments studying the effect of pH on the adsorption capacity of LZH were conducted at a pH range of 3 to 10. Initial phosphate concentration experiments were conducted after the pH experiments at initial concentrations ranging between 0.5 mg L⁻¹ and 1000 mg L⁻¹ at a fixed pH of 7. Initial and final phosphate concentrations were analyzed using a Dionex ion chromatography unit (ICS-5000+). A suitable amount of potassium monobasic phosphate, 7.17 mg, was dissolved in deionized water to produce 5 mg/L phosphate solution, which was polluted with different concentrations of humic acid (10 to 50 mg/L). Suitable amount of humic acid sodium salt is used as a competitor ions. The simulated phosphate-humic acid solution was treated BA. For each experiment, the BA and phosphate-humic acid solution were mixed at different ratios (40 to 60 g/L), then the mixture was shaken, using a bench-top shaking incubator at a speed of 100 rpm for 24 hours. The residual phosphate concentration in solution was measured by filtering a few millimeters in a 0.45µm filter and analyzed using standard phosphate cuvette tests (LCK-349 and 350) and a spectrophotometer (DR- 2800). It is noteworthy to mention that to measure the concentration of humic acid using the

spectrophotometer, a calibration curve was first developed for the concentration range 0 to 50 mg/L.

The adsorption capacity, q_t , at a specific time t and the percent removal of phosphate were calculated using the equations presented below: Chromatography System (ICS-5000)

$$q_t = (C_0 - C_t)V/W \dots\dots\dots(1)$$

$$\% \text{ removal} = (C_0 - C_t)/C_0 * 100\% \dots\dots\dots(2)$$

where, C_0 (mg L⁻¹), and C_t (mg L⁻¹) denote the initial and equilibrium phosphate concentrations, respectively, V (L) is the volume of the solution, and W (g) is the mass of the adsorbent used.

Characterization

Samples morphologies and surface elements were studied using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX). The point of zero charge (pH_{zpc}) for the adsorbent was evaluated by potentiometric titration.

Adsorption isotherm:

The relationship between the adsorbed and aqueous concentrations at the equilibrium status is very essential. Many isotherm models such as the Langmuir and Freundlich models could be used to assess this relationship. In the present study, the Langmuir model, Equation (3), has been applied to assess the relationship between the adsorbed and aqueous concentrations of phosphate not only because this model is the most widely used one, but also it delivers the required parameters to determine the separation factor (R_L), which is represented by Equation (4). The latter gives a direct assessment for the affinity between the adsorbate and adsorbent; the adsorption process is unfavorable, linear, favorable, or irreversible when $R_L > 1$, $R_L \approx 1$, $1 > R_L > 0$, and $R_L \approx 0$, respectively.

$$C_e/q_e = 1/(Q_0 * b) + C_e/Q_0 \dots\dots\dots(3)$$

$$R_L = 1/(1 + b * C_i) \dots\dots\dots(4)$$

where Q_0 and b represents the theoretical mono-layer adsorption (mg/g) and the energy of adsorption (L/mg), respectively. The values of Q_0 and b can be obtained from the plot of the Langmuir model (C_e/q_e against C_e); Q_0 and b are obtained from the slopes and intercepts of the mentioned plot, respectively. In the present study, the Langmuir model was performed by mixing 100 ml of phosphate solution with different amounts of BA (1.5 to 6.5 g/L), in airtight containers, and shaking for 24 hours at speed of 100 rpm to reach the equilibrium status. The results were plotted to get the required information to calculate R_L .

3. Analysis:

3. Batch experiments:

A batch adsorption experiment is one of the most common tests used to measure adsorption equilibrium and kinetics from solutions. It consists of the addition of a known mass of sample to a fixed volume of liquid at an initial concentration.



3.1. Adsorption isotherm:

The relationship between the initial phosphate concentration and the adsorption performance of La@BC, isotherm experiments were conducted using solutions with different initial phosphate concentrations. As shown in Fig. 4, the phosphate adsorption capacities of La@BC sharply increased as the initial phosphate concentration increased. The regression of the Langmuir model was relatively higher than that of the Freundlich model, indicating the Langmuir model was more suitable to describe the adsorption process and a monolayer adsorption process occurred on La@BC surface. The Langmuir model also showed that La@BC has a high affinity towards phosphate. According to the Langmuir model, the maximum adsorption capacity slightly lower than other La based adsorbents. But when the adsorbent capacities were calculated based on per unit of La, La@BC exhibited excellent removal capacity compared to other La based adsorbents. Given the superior removal capacity and good liquid-solid separability, the granular La@BC adsorbent can efficiently avoid appreciable problems caused by powder adsorbent due to the difficulties in solid/liquid separation process.

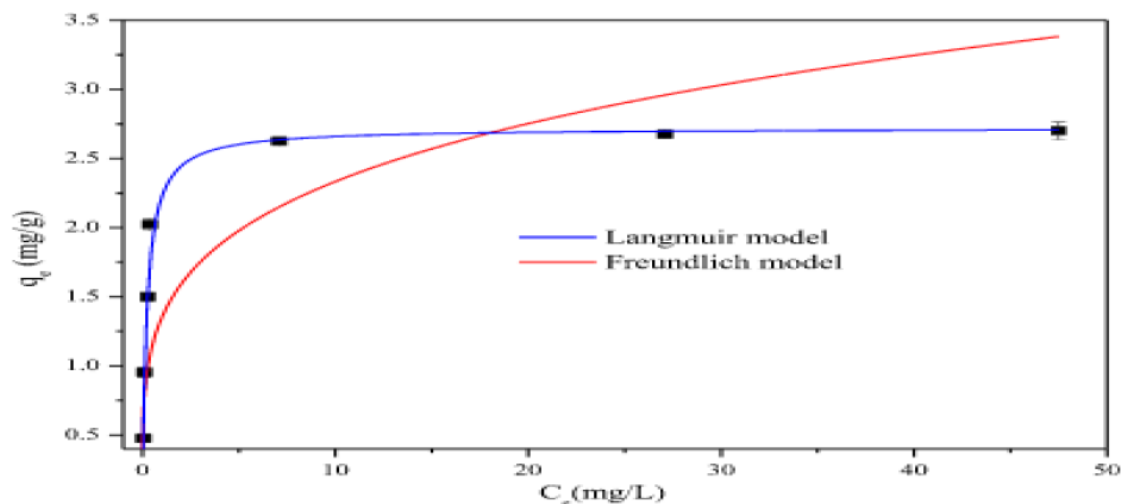


Fig. 4. the phosphate adsorption capacities of La@BC between Langmuir model & Freundlich model.

The Freundlich model provided a better description of the isotherm data relative to the Langmuir model in terms of the higher correlation coefficient. These findings suggest that the adsorption of phosphate on LZH tends towards multilayer adsorption on heterogeneous active sites rather than monolayer adsorption. This provides further evidence that electrostatic interaction between the LZH surface and the negatively charged phosphate species did not play a dominant role in the adsorption process as it becomes less effective after monolayer adsorption. The synthesized LZH in this study exhibited a significantly higher adsorption capacity for phosphate relative to the other reported adsorbents. Furthermore, LZH presented other advantages such as higher adsorption at a neutral pH, room temperature, and at a lower adsorbent dosage.



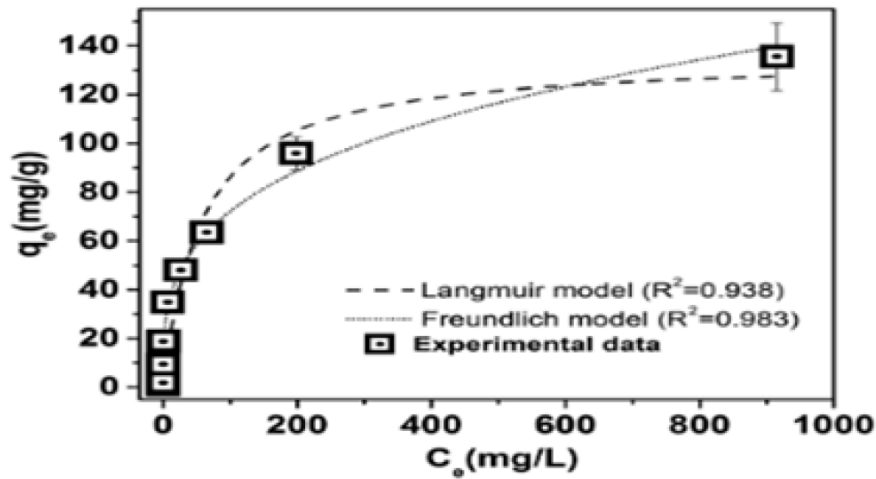


Fig. 5 Phosphate Adsorption isotherms on LZH.

As was mentioned above, assessment of the relationship between the adsorbed and aqueous concentrations is a basic step in the adsorption studies. Thus, the Langmuir model has been performed, in the present study, to assess the relationship between the adsorbed and aqueous concentrations of phosphate. Additionally, the separation factor has been calculated to evaluate the affinity between the phosphate and BA particles. Langmuir isotherm constants Q_0 and b have been calculated by plotting C_e/q_e against C_e , as depicted in Figure 6.

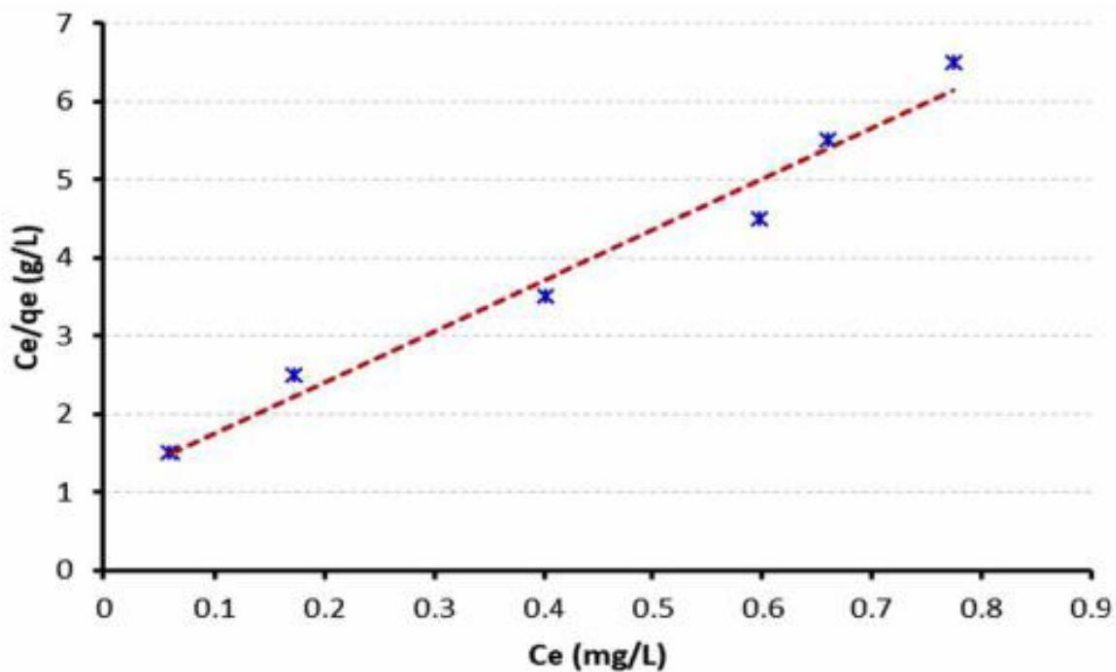


Figure- 6: Langmuir isotherm for phosphate adsorption on BA particles.

According to Langmuir isotherm constant, the adsorption of phosphate on BA particles was a favorable adsorption. The present method has an edge over many of commonly used methods for phosphate removal because it does not require a long treatment time, it does not produce



significant volumes of sludge, it helps to recycle waste in an eco-friendly way, and it does not deplete the natural resources.

Conclusions:

A new type of spherical adsorbent—La modified granular bio-ceramisite (La@BC) by co-precipitation method has been developed. La@BC exhibited excellent removal capacity. Phosphate could be efficiently removed by La@BC even under alkaline conditions. LZH was synthesized via a simple co-precipitation process that could be easily scaled up. LZH exhibited high phosphate adsorption in a synthetic solution as well as in real treated sewage effluent. LZH is a promising adsorbent for the adsorption and recovery of phosphate from water as well as for the treatment of treated wastewater effluent. BA from power plants, to remove phosphate from water in the presence of competitor ions. The BA has the potential ability to remove phosphate. Here the BA sample contains considerable concentrations of iron, aluminium, and manganese oxides, which have good ability to remove phosphate from solutions, and it was found that the best performance of the BA particles. The adsorption isotherm study evidenced a high affinity between the BA particles and phosphate. Here, i reviewed the various phosphate removal adsorbents by batch process. We know that the biological methods require long treatment time, produce high volumes of sludge with high moisture content that requires expensive management strategies, which negatively influence its cost-effectiveness. In addition, biological reactors require precise and continuous monitoring to avoid the death of the bacteria. In terms of advanced phosphate treatment methods, recent studies employed nanomaterials, such as nano-alumina, to achieve rapid and efficient phosphate removal from solutions. Although the nanomaterials demonstrated efficient removal of phosphate from solutions, the high cost of the nanomaterials and the possibility of releasing nanoparticles into the water being treated (toxicity) are the main limitations for this type of treatment method. So this review show the The Langmuir & The Freundlich model of three adsorbents & compare among the three adsorbents by adsorption process which makes tremendous effect on adsorption study.

References:

- [1] P. Koilraj, K. Sasaki, Selective removal of phosphate using La-porous carbon composites from aqueous solutions: batch and column studies, *Chem. Eng. J.* 317 (2017) 1059–1068, <https://doi.org/10.1016/j.cej.2017.02.075>.
- [2] D.D. Lucena-Silva, J. Molozzi, J.D.S. Severiano, V. Becker, J.E.D. Lucena Barbosa, Removal efficiency of phosphorus, cyanobacteria and cyanotoxins by the “flock & sink” mitigation technique in semi-arid eutrophic waters, *Water Res.* 159 (2019) 262–273, <https://doi.org/10.1016/j.watres.2019.04.057>.
- [3] M. Slaný, Ľ. Jankovič, J. Madejová, Structural characterization of organo-montmorillonites prepared from a series of primary alkylamines salts: mid-IR and near-IR study, *Appl. Clay Sci.* 176 (2019) 11–20, <https://doi.org/10.1016/j.clay.2019.04.016>.
- [4] W. Shi, Y. Fu, W. Jiang, Y. Ye, J. Kang, D. Liu, Y. Ren, D. Li, C. Luo, Z. Xu, Enhanced



phosphate removal by zeolite loaded with Mg-Al-La ternary (hydr)oxides from aqueous solutions: performance and mechanism, *Chem. Eng. J.* 357 (2019) 33–44, <https://doi.org/10.1016/j.cej.2018.08.003>.

[5] W. Xia, L. Guo, L. Yu, Q. Zhang, J. Xiong, X. Zhu, X. Wang, B. Huang, R. Jin, Phosphorus removal from diluted wastewaters using a La/C nanocomposite-doped membrane with adsorption-filtration dual functions, *Chem. Eng. J.* 405 (2021), 126924, <https://doi.org/10.1016/j.cej.2020.126924>.

[6] L. Chen, Y. Li, Y. Sun, Y. Chen, J. Qian, La(OH)₃ loaded magnetic mesoporous nanospheres with highly efficient phosphate removal properties and superior pH stability, *Chem. Eng. J.* 360 (2019) 342–348, <https://doi.org/10.1016/j.cej.2018.11.234>.

[7] X. Li, J. Chen, Z. Zhang, Y. Kuang, R. Yang, D. Wu, Interactions of phosphate and dissolved organic carbon with lanthanum modified bentonite: Implications for the inactivation of phosphorus in lakes, *Water Res.* 181 (2020), 115941, <https://doi.org/10.1016/j.watres.2020.115941>.

[8] S. Dong, Y. Wang, Y. Zhao, X. Zhou, H. Zheng, La³⁺/La(OH)₃ loaded magnetic cationic hydrogel composites for phosphate removal: Effect of lanthanum species and mechanistic study, *Water Res.* 126 (2017) 433–441, <https://doi.org/10.1016/j.watres.2017.09.050>.

[9] P.C. D'Haese, G. Douglas, A. Verhulst, E. Neven, G.J. Behets, B.A. Vervaet, K. Finsterle, M. Lüring, B. Spears, Human health risk associated with the management of phosphorus in freshwaters using lanthanum and aluminium, *Chemosphere* 220 (2019) 286–299, <https://doi.org/10.1016/j.chemosphere.2018.12.093>.

[10] H. Yin and Z. Tang, *Chem. Soc. Rev.*, 2016, 45, 4873–4891.

[11] G. Rogez, C. Massobrio, P. Rabu and M. Drillon, *Chem. Soc. Rev.*, 2011, 40, 1031–1058.

[12] A. H. Leung, S. D. Pike, A. J. Clancy, H. C. Yau, W. J. Lee, K. L. Orchard, M. S. Shaffer and C. K. Williams, *Chem. Sci.*, 2018, 9, 2135–2146.

[13] (a) A. Gordeeva, Y.-J. Hsu, I. Z. Jenei, P. H. Brant Carvalho, S. I. Simak, O. Andersson and U. Häussermann, *ACS Omega*, 2020, 5, 17617–17627; (b) T. Shinagawa, M. Watanabe, T. Mori, J.-i. Tani, M. Chigane and M. Izaki, *Inorg. Chem.*, 2018, 57, 13137–13149.

[14] (a) H. N. Tran, C.-C. Lin and H.-P. Chao, *Sep. Purif. Technol.*, 2018, 192, 36–45; (b) J. Miao, M. Xue, H. Itoh and Q. Feng, *J. Mater. Chem.*, 2006, 16, 474–480.

[15] J. Demel, J. Pleštil, P. Bezdička, P. Janda, M. Klementová and K. Lang, *J. Colloid Interface Sci.*, 2011, 360, 532–539.

[16] Kirk, D. W., Jia, C. Q., Yan, J. & Torrenueva, A. L. 2003 Wastewater remediation using coal ash. *Integrated Management of Hazardous Waste* 5, 5–

[17] Hjelmar, O., Johnson, A. & Comans, R. 2010 Incineration: Solid Residues. In: *Solid Waste Technology and Management*, Volume 1 and 2 (T. H. Christensen, ed.). John Wiley & Sons, Ltd, Chichester, UK.

[18] Zhang, B. & Poon, C. S. 2015 Use of furnace bottom ash for producing lightweight aggregate concrete with thermal insulation properties. *Journal of Cleaner Production* 99, 94–100.

[19] Shubbar, A. A., Jafer, H., Dulaimi, A., Hashim, K., Atherton, W. & Sadique, M. 2018 The development of a low carbon binder produced from the ternary blending of cement, ground



granulated blast furnace slag and high calcium fly ash: an experimental and statistical approach. *Construction and Building Materials* 187, 1051–1060.

[20] Alwash, R. S. M. 2017 Treatment of Highly Polluted Water with Phosphate Using BAPPP-Nanoparticles. MSc thesis, Environmental Engineering, University of Technology, Iraq, Baghdad, Iraq.

[21] Tyagi, S., Rawtani, D., Khatri, N. & Tharmavaram, M. 2018 Strategies for nitrate removal from aqueous environment using nanotechnology: a review. *Journal of Water Process Engineering* 21, 84–95

[22] Jamaludin, S. S., Rani, N. A. & Mohamad, N. 2019 Investigation of water absorption and strength performances on concrete bricks containing Malaysian thermal power plant coal bottom ash (CBA). *Journal of Physics: Conference Series*, IOP Publishing 1349, 1–6

[23] Liu, M., Wang, C., Guo, J., Zhang, L., 2021 Removal of phosphate from wastewater by lanthanum modified bio-ceramisite. 2021 *Journal of Environmental Chemical Engineering* 9 (2021) 106123

[24] Hashim, k., Ewadh, H, M., Muhsin, A., Zubaidi, S., Kot, P., Muradov, M., Aljefery, .and Al-Khaddar, R., 2020 Phosphate removal from water using bottom ash: adsorption performance, coexisting anions and modelling studies. *Water Science & Technology* | in press | 2020. doi: 10.2166/wst.2020.561

[25] Almasri, D., Essehli, R., Tong, Y., and Lawlera, J., Layered zinc hydroxide as an adsorbent for phosphate removal and recovery from wastewater. 2021 *Royal Society of Chemistry* DOI: 10.1039/d1ra04279c

