**Phosphate Removal from Water: A Comparison of Adsorbents**

**Abstract**

Phosphate contamination poses a significant threat to water quality, leading to harmful eutrophication and ecosystem imbalances. Effective phosphate removal is crucial to ensure the health of aquatic systems. Among various techniques, adsorption has emerged as a promising method for phosphate elimination, even at trace concentrations. This review explores the potential of three primary adsorbents—lanthanum-modified bio-ceramisite (La@BC), layered zinc hydroxide (LZH), and industrial by-products such as bottom ash (BA)—in removing phosphate from water. La@BC is particularly noted for its high efficiency and recyclability, making it a sustainable option for long-term use. LZH, synthesized through a straightforward precipitation method, shows remarkable adsorption performance due to its high surface area and unique structural properties. Additionally, BA, an affordable industrial by-product, demonstrates considerable phosphate removal capacity, offering an economically viable solution.

The paper delves into the adsorption mechanisms, key experimental variables, and desorption dynamics associated with each material. It also identifies existing research gaps, challenges, and the need for scalable, sustainable solutions. Future research directions are proposed to integrate advanced materials and innovative processes, further improving phosphate removal technologies for practical applications.

**Keywords:** Phosphate removal, adsorption process, Lanthanum-modified bio-ceramisite (La@BC), Layered zinc hydroxide (LZH), Bottom ash (BA), Adsorption isotherms, Desorption efficiency, Water purification.

**1. INTRODUCTION**

The extraction of phosphate from water poses a significant environmental danger since elevated phosphate levels cause pollution, leading to harmful algal blooms, oxygen depletion, and a reduction in aquatic biodiversity. An exhaustive evaluation of the various absorbents employed for eliminating phosphates is the goal of this research., including their modes of action, efficacy, benefits, and drawbacks. The proliferation of plants and algae is dependent upon phosphorus, a vital ingredient. Phosphate ions are present in rocks and minerals, organophosphorus pesticides, domestic wastewater, industrial effluents, and agricultural fertilizer runoff. Phosphate ions enter aquatic systems by soil erosion, rock degradation, and the excretion of animals and wildlife. Unmanaged runoff from farming operations and waste from residential and commercial establishments are the primary contributors to the elevated phosphate levels in water sources. Lanthanum (La) is a rare metal that exhibits chemical stability and is environmentally benign. Significant attention has been devoted to it because of the high binding of La3+ to phosphate.

La can generate a consistently weakly soluble precipitate upon interaction with PO3 [1]. The effectiveness of lanthanum-based adsorbents in removing phosphates from wastewater and avoiding excessive mineral formation in aquatic ecosystems has led to their increased popularity. These adsorbents include zeolite, carbon fiber, mesoporous silica, and lanthanum-modified bentonite [2-6].

In various weather conditions, La-based adsorbents are more effective in eliminating phosphates than Al and Fe elements. [7,8]. It did not have a substantially detrimental impact on people or other species present in the environment [9]. Numerous varieties of stacked sheet-like materials exist. Under this broad heading, Under this broad heading, you may find both layered single-metal hydroxides (LSHs) and layered double-metal hydroxides (LDHs).

the latter has two metal cations embedded within its host layer. Natural crystal brucite is an architectural inspiration for LMHs. It is composed of layers of metal hydroxyls interspersed with anions that balance the charges. The simplicity of LMHs in terms of creation, modification, and organization has led to their meteoric rise in popularity over the last decade [10]. Because of their malleability, they find use in a wide variety of products, including those that prevent fires, thin film electronics, energy storage and conversion, catalysis, magnetism, and adsorption/ion exchange [10, 11]. Layered zinc hydroxides (LZHs) are a subset of LSH.

As an intercalated ion like sulfate, carbonate, nitrate, or carboxylate, the formula is Zn5(OH)8(A)2$nH2O [12]. In its entirety, the structure is made up of zinc hydroxide layers that contain zinc ions arranged in octahedral and tetrahedral patterns [13]. To counteract the laminates' positive charge, the interlayer anions are exchangeable anions. For this reason, LZHs are very good in exchanging anions [13,14]. With the addition of Zn and other metals, LZHs may be transformed into LDH salts; they are easy to synthesis, have a higher anion-exchange capacity than LDHs, and [15]. Bottom Ash, or BA, mostly consists of solid and non-combustible particles that remain at the base of the combustion chamber due to their weight and size. Despite the abundance of iron and aluminum oxides in BA, the majority is relegated to landfills, incurring substantial expenses in terms of land use and transportation [16,17].

Owing to its advantageous chemical composition and accessibility, BA has been attempted to be recycled in some contexts, such as the concrete industry [18,19]. Nonetheless, pure BA in power plants has not yet been used for water purification. Little is known about the efficacy of BA Nano powder for water purification. Additionally, the production of Nano powders is prohibitively costly and presents safety concerns, rendering them applicable in only a few scenarios. BA served as an economical phosphate adsorbent for our study. Two significant considerations justify the selection of the BA in this context: Initially, the BA had a considerable capacity for phosphate absorption due to its high content of iron and aluminum oxides, as shown in the study's findings [20,21].

Furthermore, the BA is an industrial byproduct detrimental to the environment, often necessitating costly operational strategies [22-26]. Utilizing this waste product for water treatment is advantageous for both the environment and the economy. The primary objectives of this study are to (1) perform an extensive characterization of an anion removal adsorbent utilizing diverse characterization techniques; (2) investigate the adsorption efficacy of phosphate using artificial water, including deposition rates, the effect of acidity, isotherms during desorption, and the impact of co-existing ions; (3) evaluate various phosphate removal techniques and methodologies; and (4) propose potential mechanisms for phosphate removal. This paper will discuss several phosphate-based adsorbents.



**Figure-1:** Phosphorus Cycle Illustrating Transport (Input and Uptake) Between Terrestrial and Aquatic Ecosystems.



**Figure-2:** Algal bloom, caused by phosphorus pollution of water.

**2. MATERIALS & METHODS**

**2.1 Materials**  
Biochar is a solid material which is generated through the pyrolysis of sewage sludge. The process involves the use of zinc acetate (Zn(OAc)2) and sodium hydroxide (NaOH).

**2.2 Adhesion of La-modified granular adsorbent (La@BC)**

**(1) Formulation of Granular Bio-Ceramisite (BC):** Here, an assortment of biochar fly ash (100 g, in a 2:8 mass ratio) was used to form approximately spherical pellets which have a diameter of 8-12 mm. This was achieved by adding 80mL of distilled water and granulating the mixture. The pellets were made moisture less at 105ºC in an oven until a constant weight was reached. Subsequently, the dried pellets were fired at 1100ºC for 30 minutes in a laboratory-scale electric furnace, resulting in the formation of BCs [27].

**(2) Adhesion of La@BC:** La@BC adsorbents were synthesized through a co-precipitation method. To prepare a 2 wt% La solution, 5.347 g of LaCl₃·7H₂O (analytical grade) was dissolved in 100 mL of distilled water in a 200 mL beaker. Subsequently, 100 g of BCs were soaked in the LaCl₃ solution and stirred continuously at 120 rpm for 4 hours. Subsequently, a NaOH solution (0.1 mol/L) was gradually added to the mixture to adjust the pH to 10. The solution was stirred for an additional 2 hours, after which the modified La(OH)­3 products were rinsed with distilled water until no chloride ions were detected (confirmed by the AgNO3 titration method). Finally, the material was dried at 60ºC for 4 hours and then heated at 300ºC for 30 minutes in an electric furnace to produce the La@BC adsorbents [28-32].

**2.3 Synthesis of LZH**

LZHs were synthesized via a precipitation process using zinc acetate and NaOH. A solution of zinc acetate (20 g in 600 mL deionized water) was mixed with a NaOH solution (5g in 100 mL deionized water) and added dropwise until the pH stabilized at 7. The mixture was stirred at 45ºC and 400 rpm for 24 hours. The obtained slurry passed through a 0.45 mm filter, thoroughly washed with deionized water, and dried at 90°C [33-35].

**2.4. Batch Experiments**

Within this study, reagents were of analytical grade. The preparation of Phosphate stock solutions with 1g P/L was done by using KH2PO4 and distilled water and as well as the working solutions of varying phosphate concentrations were obtained via dilution. Initial pH adjustments were made with 0.1 mol/L HCL or NaOH. The residual phosphate concentrations in the solutions were analyzed using the ammonium molybdate spectrometric method. Batch experiments were conducted in triplicate to ensure accuracy and reliability. The reusability of La@BC for phosphate removal was examined through five sequential adsorption-desorption cycles. Given the strong dependence of desorption efficiency on pH, a 1 mol/L NaOH solution was utilized as the regenerating agent.

Collection of La@BC adsorbents

The sample was transferred to a 200 mL Erlenmeyer flask containing 100 mL of NaOH regenerant and stirred continuously at 120 rpm / 350 rpm24h

The reusable adsorbents were regenerated. Constant stirring of 120 rpm/350rpm 24h

**Figure-3:** Flow chart about phosphate removal by Batch process using La@BC adsorbents

0.5 g L1 adsorbent +5 mg L1 phosphate solution

pH was modified using 0.1–1 mg L1 HCl or NaOH solutions.

transferred in polyethylene centrifuge tubes as well as shaken at a rate of 350 rpm using a mechanical shaker table.

**Figure-4:** Flow chart about phosphate removal by Batch process using LZH adsorbents

Mixing of the BA, along with phosphate-humic acid solution at diverse ratios (40 to 60 g/L)

Shaking, using a bench-top shaking incubator 100 rpm speed 24hours.

Measuring phosphate concentration by filtering

**Figure-5:** Flow chart about phosphate removal by Batch process using BA adsorbents.

The effects of contact time, pH, phosphate concentration, and other ions on the adsorption process has been studied. All the experiments were conducted at room temperature and repeated twice to get reliable results. For the initial tests, different amounts of LZH, from 0.5 to 200 g/L has been tried. Based on what is found, 0.5 g/L turned out to be the best balance of effectiveness and cost, so, that amount for the rest of the experiments was used. To analyze the results, core-level spectra and calibrated energy positions using a standard C–C signal has been recorded. The measurement of the zeta potential of the material with a Malvern Zetasizer Ultra, and for phosphate and other anions has also been done, a Dionex Ion Chromatography System was used. The effect of pH by varying it between 3 and 10 was tested and once the ideal pH of 7 was found, the experiment moved on to experiments with phosphate density varying between 0.5 mg/L to 1000 mg/L. The phosphate solution was made by dissolving potassium monobasic phosphate in deionized water. Humic acid in concentrations between 10 and 50 mg/L, using its sodium salt form as the competing ion was also added. For every analysis, the phosphate-humic acid solution with BA adsorbent in different ratios (40–60 g/L) was mixed. These mixtures were shaken for 24 hours in a shaker at 100 rpm. Afterward, the solutions were processed through a 0.45 μm filter, and measured the phosphate levels with a spectrophotometer using standard phosphate tests. Humic acid concentration in the range of 0–50 mg/L was determined using a calibration curve.

Here the following equations have been used to determine the qt, at a specific time t, adsorption capacity as well as the percent removal of phosphate.

|  |
| --- |
| Where,  Co­= initial phosphate concentrations (mg/L),  Ct= equilibrium phosphate concentrations (mg/L),  V= volume of the solution (L) |

--------------- (1)

% removal= × 100% -------------- (2)

* 1. **Characterization**

The surface and elements of the samples were studied through the use of Scanning Electron Microscopy (SEM) along with Energy-dispersive X-ray spectroscopy (EDX). Potentiometric titration was done to serve the purpose of zero charge (pHzpc) of the adsorbent.

* 1. **Adsorption Isotherm**

The balance between what gets adsorbed and what stays in the solution at equilibrium is key to understanding the process. To figure this out, researchers use models like Langmuir and Freundlich. For this study, the Langmuir model was picked because it’s widely used and provides valuable parameters. One of these parameters is the separation factor (Rᵥ), which can be calculated with the following equations. This factor shows how well the adsorbent and adsorbate interact. If Rᵥ is over 1, the adsorption isn’t favorable. When it’s exactly 1, the process is linear. If it falls between 0 and 1, it’s favorable, and when it hits 0, it’s irreversible.

|  |
| --- |
| Where,  Qo= theoretical mono-layer adsorption (mg/g),  b= the energy of adsorption (L/mg) |

From the Langmuir model plot ( versus Ce), the values for Qo​ and b are determined; where the slope and intercept provide these parameters. In the current investigation, by combining 100 mL of phosphate solution with different amounts of BA (ranging from 1.5 to 6.5 g/L) in sealed containers, the Langmuir model was examined. These mixtures were agitated at 100 rpm for 24 hours to reach equilibrium. The data collected was then used to create the plot and calculate RL.

**3. RESULTS AND DISCUSSION**

**3.1 Batch experiments**

It is common practice to test many solutions' bonding behavior and stability in a single batch exposure experiment. It involves adding a known amount of sample to a set amount of liquid with a certain quantity.

**3.2 Adsorption Isotherm:**

In order to determine the effect of beginning phosphate level on the binding capabilities of Lanthanum modified granular bio-ceramicist, we conducted isotherm tests with liquids containing varied amounts of phosphate ranging from 1 to 100 mg P/L.

Figure 6 shows that the capacity of lanthanum-modified granular bio-ceramicists to take in phosphate increased rapidly from 1 mg P/L to 10 mg P/L, after which it remained constant from 10 mg P/L to 50 mg P/L. Compared to the Freundlich model, which failed to adequately describe the adsorption process, the Langmuir model performed better in terms of regression (R2 =0.987). The surface of the granular bio-ceramicist treated with lanthanum underwent a monolayer adsorption process. Additionally, the Langmuir model demonstrated that lanthanum-modified granular bio-ceramicist adheres very well to phosphate. The greatest adsorption capacity of 2.719 mg P/g is somewhat lower than other La-based adsorbents, according to the Langmuir model. The most important factor is that our 2% concentration of La modification agent was much lower compared to previous La-changed materials. This is in contrast to the 10–70% that have been reported. Since there were fewer La ions accessible, the adsorption capacity of the lanthanum-modified granular bio-ceramicist adsorbent was reduced. Lanthanum-modified granular bio-ceramicist outperformed other La-based adsorbents in terms of removal capacity (136 mg P/g La) when adsorbent capacities were calculated according to La concentration. To circumvent the major issues that powder adsorbents encounter while attempting to separate solids and liquids, the grainy lanthanum-modified granular bio-ceramicist adsorbent is superior at removing substances and separating liquids and solids.

**Figure 6:** Adsorption isotherms of phosphate onto La@BC

(Initial phosphate concentrations: 1–100 mg P/L; adsorbent dose: 20 g/L; pH: 7.0 ± 0.2; contact time: 24 h).

Adsorption isotherms of phosphate on LZH are shown in Figure 7

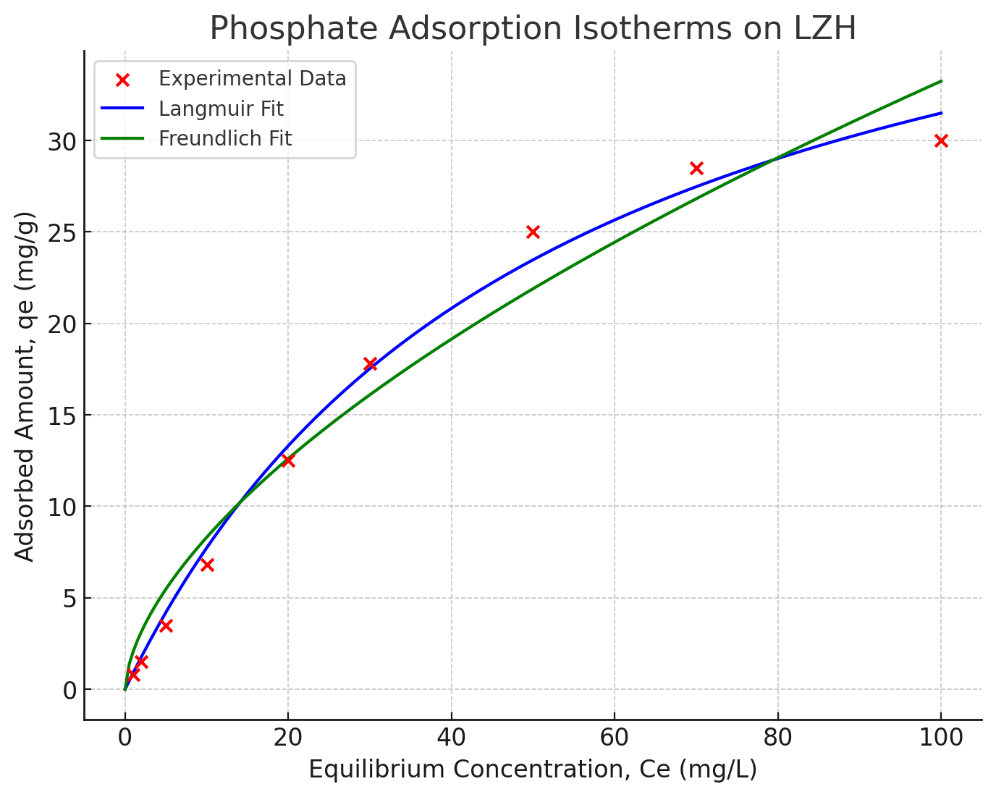


Figure 7: Phosphate Adsorption isotherms on LZH.

Based on the findings, it was found that the Freundlich model (R² = 0.983) was more accurate in representing the isotherm data than the Langmuir model (R² = 0.938). This indicates that, instead of a single homogeneous layer, phosphate adsorption onto LZH is probably the result of multilayer interactions at diverse active sites. Also, once the first monolayer was formed, the electrostatic interactions between the negatively charged phosphate species and the LZH surface were less important in the adsorption process, according to the results.   
Phosphate adsorption seems to have permeated the interstices between the layers of the structure, suggesting that it went beyond the surface itself. The synthesized LZH stood out from other adsorbents described in the literature due to its much greater phosphate adsorption capability. It also has other advantages, such as working well at room temperature, with a reduced amount of adsorbent, and in settings of neutral pH.

Table 1 summarizes the model parameters and Pearson coefficients for the adsorption isotherm that were derived by fitting the experimental data to the Freundlich and Langmuir models.

The characteristics of the Freundlich and Langmuir isotherms for phosphate adsorption on LZH are recorded in Table 1.

Table 1: The recorded characteristics of the Freundlich and Langmuir isotherms for phosphate adsorption on LZH

|  |  |
| --- | --- |
| **Equilibrium Adsorption Models** | **LZH** |
| **Langmuir** |  |
| *Xm(mg.g-1)* | 135.4 |
| *b* | 0.0175 |
| *R2* | 0.938 |
| **Equilibrium Adsorption Models** | **LZH** |
| **Freundlich** |  |
| *Kf (mg/g(dm3/g-1) n)* | 18.19 |
| *1/n* | 0.299 |
| *R2* | 0.983 |

As highlighted earlier, a key aspect of adsorption studies involves examining the relationship between the concentration of the adsorbed and aqueous phases. In this study, the Langmuir model was applied to explore this relationship for phosphate adsorption. To further evaluate the interaction between phosphate and BA particles, the separation factor was calculated. A plot of Ce/qe vs Ce was used to estimate the Langmuir isotherm constants, Qo and bb. This process is shown in Figure 8.

Figure 8: Langmuir isotherm for phosphate adsorption on BA particles.

Values of 6.522 mg/g for Qo and 0.14 L/mg for b were determined. A phosphate adsorption R L value of 0.417 was determined for the BA particles using Equation (8) and the predicted Langmuir isotherm constant. Phosphate adsorption on BA particles was clearly successful, as this demonstrated. The study's results show that this method is better than many others used to remove phosphate because it doesn't need a long treatment time, doesn't make a lot of sludge, recycles waste in an eco-friendly way, and doesn't use up natural resources. One popular way to get rid of phosphate, according to the research, is to use biological reactors. These reactors are very good at getting rid of phosphate up to 99% effective. Biological ways, on the other hand, take a long time to treat and make a lot of sludge with a lot of water in it, which needs expensive handling techniques that make it less cost-effective. Also, biological tanks need to be carefully and continuously watched so that the bacteria don't die. Recent studies have used nanoparticles, like nano-alumina, to quickly and effectively remove phosphate from liquids. These are examples of more advanced ways to treat phosphate. The nanomaterials were good at getting rid of phosphate from solutions, but they are very expensive and could release harmful nanoparticles into the water that is being treated. These are the major problems with this type of treatment.

**4. CONCLUSION**

The co-precipitation approach was used to synthesize a novel spherical adsorbent known as Lanthanum-modified granular bio-ceramicist. Lanthanum modified showed exceptional efficacy in eliminating substances, Lanthanum demonstrated excellent phosphate removal even under acidic circumstances. Due to its diminutive particles, Lanthanum modified proved effective in separation. Liquids and solids were much more effective in eliminating phosphates compared to alternative powdered adsorbents.

The presence of ions Cl-, NO3-, HCO3-, and SO4^2- had no impact on phosphate removal, indicating that La@BC exhibits a high selectivity for phosphate. A straightforward co-precipitation technique was used to synthesize LZH, facilitating the production of larger quantities. LZH was shown to effectively absorb significant amounts of phosphate in both a synthetic solution and actual treated sewage effluent. Researching LZH before to phosphate absorption, after phosphate absorption, and after phosphate recovery revealed that phosphate could be effectively absorbed and recovered on LZH while maintaining its structural integrity. This research demonstrates that LZH is a viable material for phosphate removal from water, phosphate recovery, and the treatment of previously treated wastewater. This research aimed to determine if industrial waste (BA from power plants) could effectively eliminate phosphate from water in the presence of competing ions.

The first phase of the project was examining the chemical and physical characteristics of the BA to determine its potential for phosphate removal. This included assessing the concentrations of iron and aluminum oxides, in addition to evaluating its surface area and density. Subsequently, a series of batch experiments were conducted in diverse environments to demonstrate its capacity to eliminate phosphate. The Langmuir isotherm model was used to investigate the kinetics of the adsorption process. The study's findings indicated that the BA sample contains significant quantities of iron, aluminum, and manganese oxides, all of which effectively eliminate phosphate from solutions. The BA particles exhibited optimal performance in acidic solutions with elevated BA concentrations and at standard to moderate temperatures (up to 35°C).

The adsorption isotherm analysis indicated a significant affinity between the BA particles and phosphate. I discussed several adsorbents for phosphate removal using a batch approach.   
What methods may be used to eliminate phosphate in a batch process? Demonstrate the functionality of the Langmuir and Freundlich models for various adsorbents. I will compare the three adsorbents based on their mechanisms of action.

**Statements and Declarations**

**Data availability:** The authors declare that the data supporting the findings of this study are available within the article. No new data were generated during the study.

**Ethical approval:** Not applicable.

**Informed consent :** Not applicable.

**Consent to Publish declaration**: Not applicable

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