

Journal of Sustainable Development of Energy, Water and Environment Systems

http://www.sdewes.org/jsdewes



Year 2026, Volume 14, Issue 1, 1130640

Original Research Article

Simultaneous Recovery of Ammonium and Phosphate from Wastewater Using Magnesium-Activated Temple Waste Biochar

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Cite as: Wijaya, I. M. W., Sumantra, I. K., Suena, N. M. D. S., Ahire, K. D., Nalawade, P. M., Simultaneous Recovery of Ammonium and Phosphate from Wastewater Using Magnesium-Activated Temple Waste Biochar, J.sustain. dev. energy water environ. syst., 14(1), 1130640, 2026, DOI: https://doi.org/10.13044/j.sdewes.d13.0640

ABSTRACT

Nutrient pollution from ammonium and phosphate in wastewater presents serious environmental challenges, including water europhication and resource inefficiency. The study aimed to analyse how magnesium-activated biochar made from temple waste could be used as a sustainable material for adsorping nutrients at the same time. The biochar was synthesized through pyrolysis and magnes um chloride activation, then applied to real wastewater from stabilization ponds in Bali. The adsorption dynamics for both ammonium and phosphate were consistent with pseudo-second-order models, suggesting that chemical absorption was the prevailing mechanism. The Freundlich isotherm model provided the best fit, suggesting heterogeneous multilayer adsorption. Results demonstrated that adsorption capacity and rate varied across different wastewater sources, with the highest adsorption rates corresponding to ponds exhibiting more towourable surface interactions. Importantly, the adsorption rate constant for phosphate surpassed that of ammonium in some cases, emphasizing the influence of ionic properties and biochar surface heterogeneity. The results confirm that biochar made from waste can effectively recover nutrients and should be included in circular approaches for managing wastewater.

KEYWORDS

Adsorption, Biochar, Nutrient Recovery, Magnesium-Activated Biochar, Wastewater, Ammonium, Phosphate, Circular Economy.

INTRODUCTION

Elevated levels of nutrients like ammonium (NH₄⁺-N) and phosphate (P) are causing water eutrophication, which is a critical worldwide concern affecting both aquatic environments [1] and human well-being [2]. These essential nutrients play a crucial role in agricultural output,

making a major contribution to the growth of algae and reduction of oxygen levels in bodies of water, ultimately causing disturbance to the natural balance of the environment [3]. Effective removal and recovery of ammonium and phosphate from wastewater are critical [4] not only for mitigating eutrophication but also for addressing the growing demand for sustainable nutrient management in agriculture[5]. Achilleos et al. [6] Investigating struvite precipitation as a method for nutrient recovery from wastewater, Koulouri et al. [7] discovered that nitrogen and phosphorus can be enriched in biochar through a process of adsorption and precipitation, Dewi & Masduqi [8] demonstrated the effectiveness of the crystallization process using silica sand media for removing phosphate, Pinelli et al. [9] focuses on developing an ion exchange process for recovering ammonium from wastewater, and Muscarella et al. [10] [10] demonstrated the efficacy of ammonium adsorption using modified zeolite. Amany these, adsorption is currently viewed as a very effective method as showed by [11] mainly due to its simplicity [12], as well as its ability to recover effectively [13], and the opportunity for regenerating the adsorbent [14]. Goldschmidt & Buffam [15], reported that the addition of biochar can increase nutrient retention in the environmental system. Susilawati et al.[16], devised a zeolite and activated charcoal-based filter material from cocoa waste that effectively absorbs ammonia. Ribeiro et al. [17] researched hybrid magnetic nanocomposites that have the capability to enhance nutrient recovery in wastewater. However, these conventional approaches often face challenges such as high operational costs, limited scalability, and inefficiencies in treating highly concentrated wastewater [18] Ni et al. [19] demonstrate that iron-modified biochar exhibits superior performance in nitro en and phosphorus recovery. Zhang et al. [20] optimized the regeneration of zeolite and reported an increase in nitrogen removal efficiency. Markou et al. [21] emphasize that the use of natural zeolite can serve as a sustainable alternative, although the cost remains high on a large scale.

Biochar is a carbon-rich material produced by processing organic matter in low-oxygen combustion conditions. It is an alternative for an affordable and eco-friendly solution for adsorpent material in order to recovering nutrients from wastewater for agricultural use. Its extensive surface area and porous composition make it ideal for effectively adsorping ammonium and phosphate ions. Barbhuiya et al. [22], affirm that the use of biochar aligns with the principles of circular economy. Shi et al. [23], explored the inorganic compound content in biochar that could be reutilized. Yang et al. [24] reported that utilizing biomass waste as biochar enhances resource value and reduces waste disposal to landfills. Meanwhile, Erdem [25], uncovered that activation with magnesium enhances the surface reactivity of biochar and creates more binding sites for nutrient ions. Further, Bolan et al. [26] assert that magnesium-activated biochar can improve soil health and microbial balance, making it more environmentally friendly. These evidence illuminate that magnesium activation is an effective strategy for enhancing adsorption efficiency and environmental sustainability..

The present study is centred on combining temple waste, coconut husks, and wood in a digestion process, along with developing and evaluating a biochar enriched with magnesium produced from these materials. There is a significant amount of biodegradable materials that can be used as inputs for the process, yet they are not fully utilized, offering a sustainable alternative for converting waste into resources. Unlike previous studies that primarily investigated the adsorption of either ammonium or phosphate individually [27], current research explores the simultaneous recovery of both nutrients, addressing a critical gap in the existing literature[28]. Hofmann et al. [29], analyzed the potential for nutrient recovery from wastewater using an adsorption kinetics approach. Panasiuk [30], examined the mechanism of phosphorus removal using magnetite as the foundation for developing an isotherm model. Moreover, Silva et al. [31], analyzed the nutrient recovery capacity using microalgae in wastewater systems..

Several previous studies have served as a crucial foundation for the present resarch, such as Wu and Vaneeckhaute [3], who examined nutrient recovery technologies from wastewater and emphasized the superiority of adsorption as a simple yet effective method. Achilleos [6]

highlighted struvite precipitation not only as a waste treatment technique, but also as a circular economic opportunity. Koulouri [7] demonstrated that biochar from fecal waste can be enriched with nitrogen and phosphorus to support nutrient recycling. Gong [32] proved that modified biochar has a higher ability to adsorb ammonium compared to phosphate. Meanwhile, Jiang [33] asserted that magnesium-based biochar characteristics heavily influence the adsorption capacity of nitrogen and phosphorus from wastewater.

The urgency of recovering phosphorus is underscored by its finite availability as evidenced by [34], and escalating demand in agriculture[35]. The traditional dependence on mined phosphate rock should be replaced by a more sustainable material balance that can equally supply the demand for phosphates. Likewise, nitrogen emission from agricultural runoff leads to agricultural and environmental inefficiencies [36]. By integrating nutrient recovery into wastewater treatment, the present study not only tackles water pollution but also offers a sustainable pathway for producing nutrient-enriched biochar as a fertilizer substitute [37]. Such innovations hold promise for reducing dependence on non-renewable resources [88] and enhancing agricultural productivity[39]. The study supports global sustainability goals related to decreasing waste, increasing resource recovery, and encouraging green technologies. Through novel biochar technologies, the investigation leads to efficient, up-scalable and sustainable wastewater treatment systems. Finally, it highlights the promise of circular economy as an effective response to environmental challenges and a driver for sustainable development.

Unlike previous study by Wijayta that tested the performance of biochar on synthetic waste under controlled laboratory conditions [40], the present research introduces novelty by examining magnesium-activated biochar derived from temple waste directly on real wastewater from four stabilization ponds in Bali. The use of real wastewater allows for the identification of the impact of heterogeneous waste composition on adsorption capacity and rate, a factor not extensively explored in previous studies. Additionally, the study emphasizes the optimization of biochar activation conditions across varying pH levels, resulting in biochar with more stable and sustainable adsorption performance. Hence, the findings not only strengthens the scientific foundation regarding the mechanisms of dual adsorption of ammonium and phosphate but also presents a solution based on local wisdom within the framework of a circular economy, relevant for sustainable waste management in tropical tourism regions.

METHODS

A laboratory experimental method was adopted to assess how well magnesium-activated biochar made from temple waste can remove ammonium and phosphate from wastewater. The main protedures included biochar preparation, activation, batch adsorption tests, and analytical evaluation. Each step is described in the following sections.

Preparation of Magnesium-Activated Temple Waste Biochar

The biochar was created using refuse-derived fuel made from ceremonial temple waste materials. The raw materials underwent cleaning, drying, and grinding to achieve consistent particle dimensions. These processed materials were formed into briquettes and subjected to thermal decomposition in a controlled-atmosphere furnace at 500 °C for two hours with restricted oxygen supply to achieve thorough carbon conversion. The next step involved activating the biochar with a solution of magnesium chloride (MgCl₂) at a concentration of 200 mg/L. The optimum pH was determined by the experiment of biochar activation with various pH, such as pH 5, 7 and 9. Each pH buffer received a 1 gram sample of biochar, with the concentration of MgCl₂ being determined through the use of Ethylenediaminetetraethanoic acid (EDTA) sodium salt at a pH range of 8 to 9. The biochar was activated under ideal pH conditions for subsequent adsorption testing. The mixture was subjected to constant stirring for

24 hours at room temperature to facilitate the integration of magnesium at the ideal pH. Further, the biochar was filtered to separate it, washed with distilled water to remove any leftover magnesium chloride, and dried at 105 °C for 12 hours until reaching a constant weight. The magnesium-infused biochar was placed in airtight containers for later usage.

Batch Experiments

Wastewater samples used in the studywere taken from stabilization ponds at the local wastewater treatment plant in the south of Bali Island, Indonesia. The stabilization ponds are utilized to treat the domestic wastewater from hotels surround. The wastewater collected from these ponds typically contains elevated concentrations of nutrients, including ammonium (NH₄⁺) and phosphate (PO₄³⁻), which are the target contaminants. Approximately 2 litres of wastewater were collected from four different stabilization ponds (Pond 1, Pond 2, Pond 3, and Pond 4) to examine the variation in nutrient concentrations. The wastewater samples were filtered to remove larger particulates before performing the adsorption experiments.

A constant activated biochar mass of 0.5 grams was added to 250 mL of the wastewater samples in each beaker. The adsorption process was monitored at two different contact times: 30 minutes and 60 minutes. The mixture was shaken at a constant speed (80 rpm) to ensure uniform distribution of biochar throughout the solution. After the sorption experiments, the biochar was filtered to be isolated. The levels of ammonium and phosphate in the solution were measured using UV-Vis Spectrophotometry following established protocols. The concentration analysis of ammonium and phosphate was performed in accordance with APHA (American Public Health Association) (2017) [41] guidelines to ensure accuracy and comparability at the international level. Spectrophotometric measurements were calibrated using standard solutions, and quality control procedures such as duplicate testing and blank utilization were implemented to minimize the potential for analysis errors. Further, method validation was performed through replicate testing, internal standard utilization, and blank testing to ensure the reliability of measurement outcomes.

Research Flow

Figure 1 presents a general overview of the research methodology which illustrating the overall flow of the experiment including sample collection, biochar preparation, activation, adsorption testing, and data analysis. The research procedure consisted of several stages, including wastewater sampling from the stabilization pond, biochar preparation using temple waste, biochar activation with magnesium chloride, and batch adsorption testing for ammonium and phosphate. Laboratory analysis was performed using UV-Vis spectrophotometry (APHA (American Public Health Association), 2017), followed by data modeling through isotherm and kinetic approaches, and final biochar characterization using Scanning Electron Microscopy (SEM)..

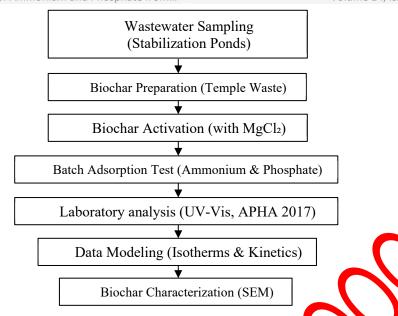


Figure 1. Schematic diagram of the research flow

<u>Figure 1</u> presents a schematic representation of the research flow that illustrates the experimental procedure, encompassing the collection of wastewater samples, preparation of biochar, activation, adsorption testing, data analysis, and characterization.

Analytical Equation

The biochar's ability to adsorb ammonium or phosphate per unit mass was referred to as adsorption capacity (q_e) which was calculated using the equation 1 provided:

$$q_e = \frac{(C_0 + C_0) \times V}{m} \tag{1}$$

The adsorption capacities were determined for both ammonium and phosphate in each stabilization pond sample, and the results were compared across different contact times (30 and 60 minutes). The rate of adsorption correlates to how quickly the biochar adsorbs the adsorbate (ammonium or phosphate). The adsorption rate constant (k) was calculated using the second-order kinetic model. The mathematical expression for the model is given as in equation 2:

$$\frac{1}{(q_t - q_e)} = \frac{1}{k} x t + \frac{1}{q_e}$$
 (2)

The absorption data for both ammonium and phosphate was analyzed using isotherm models to assess the adsorption equilibrium and capacity of biochar. Two commonly applied theoretical frameworks were utilized: Langmuir and Freundlich. The Langmuir framework is based on the premise of single-layer adsorption occurring on a surface containing a limited number of binding sites. In this case, the Langmuir adsorption equation can be expressed as in **Equation 3**:

$$\frac{1}{q_e} = \frac{1}{Q_m x \, K_L} \, x \, \frac{1}{C_e} + \frac{1}{Q_m} \tag{3}$$

The Freundlich model accounts for adsorption on heterogeneous surfaces with site-specific energy variations. It is defined by the **equation 4**:

$$q_e = K_f \times C_e^{\frac{1}{n}} \tag{4}$$

The selection of Langmuir and Freundlich isotherm models is based on their relevance in explaining the mechanism of nutrient adsorption. The Langmuir model emphasizes monolayer adsorption processes on homogeneous surfaces, while the Freundlich model is more suitable for heterogeneous surfaces with variations in binding energy Similarly, first-order and second-order kinetic models are used to evaluate adsorption rates, with the second-order model often indicating the involvement of chemisorption mechanisms. Two models were applied to analyze the obtained data from the adsorption tests in order to determine the capacity and strength of adsorption for ammonium and phosphate. The model that best matched the collected data was chosen for further investigation.

The research focused on studying the motion of ammonium and phosphate absorption by using both initial order and secondary order motion models. In accordance with the initial order motion model, the speed of absorption is linked to the variation in concentration of the adsorbate over time. The formula for the initial order motion model is as shown in equation 5 below:

$$\ln(C_0 - C_t) = \ln(C_0) - k_1 x t$$
(5)

The second-order kinetic was used to explain the adsorption process [42], showing that the rate of adsorption is equal to the square of the adsorbate concentration[43]. The equation can be found in the adsorption rate portion mentioned in **equation 2**. The second-order model is preferable in cases where the adsorption process is influenced by chemisorption. Based on the R² values of both models, the most suitable model was determined for both ammonium and phosphate adsorption[44]. Statistical regression methods were applied to examine the experimental findings for ammonium and phosphate uptake to establish the rate constants (k) and equilibrium adsorption capacities (qe). The correlation coefficients (R²) derived from evaluating the Langmuir and Freundlich isotherms, as well as the first-order and second-order kinetic frameworks, were employed to assess the precision of the model fitting[45]. The theoretical model with the highest R² coefficient was considered the most precise explanation of how nutrients are adsorbed. A Scanning Electron Microscopy (SEM) study was conducted to investigate changes in the surface texture and structural features of the biochar before activation, during activation, and after the adsorption procedure.

Although seanning electron microscopy (SEM) provides a visual representation of biochar morphology and porosity, other characterizations such as Fourier Transform Infrared Spectroscopy (FTIR) and Brunauer-Emmett-Teller (BET) surface area analysis are commonly used to assess functional groups and specific surface area. The present study prioritizes SEM due to its focus on changes in morphological structure, while further research is recommended to integrate FTIR and BET for a more comprehensive understanding of adsorption mechanisms.

RESULTS AND DISCUSSION

The following section presents the experimental results concerning the development, activation, and effectiveness of magnesium-activated biochar made from temple waste in the removal of ammonium and phosphate from wastewater. The findings have been categorized into various subsections, including the activation process of biochar, its efficacy in nutrient adsorption, modeling of kinetics and isotherms, capacity and rate of adsorption, and morphological analysis using Scanning Electron Microscopy.

Biochar Activation

According to Figure 2, the graph depicting magnesium concentration over time during the biochar activation process under different pH environments (pH 5, pH 7, and pH 9) reveals distinct trends in magnesium retention. At pH 5, the magnesium concentration starts at approximately 190 mg/L, with a rapid decline observed within the first 20 minutes, ultimately stabilizing around 110 mg/L by the 90-minute mark. A similar initial drop is observed at pH 9, where the concentration decreases sharply in the early stages but shows a recovery, stabilizing at approximately 130 mg/L by the end of the process. In contrast, at pH 7, the magnesium concentration shows a more gradual decline initially, followed by a steady increase towards the latter stages of the activation process, reaching approximately 130 mg/L by the end of 90 minutes.

The sharp initial decline in magnesium concentration observed at pH 5 and pH 9 suggests that biochar activation at these pH levels leads to a significant early-stage uptake or adsorption of magnesium. These early decrease could be attributed to the biochar's increased adsorption performance at low and high pH levels, where the ion exchange rates are higher in the initial stages of activation. However, the rate of change slows considerably after the first 20 minutes, indicating that the biochar reaches a saturation point for magnesium adsorption.

The fluctuation in magnesium concentration during the activation process at different pH levels is illustrated in <u>Figure 2</u>. The image demonstrates the variation in magnesium retention over time at pH 5, 7, and 9, indicating distinct activation patterns.

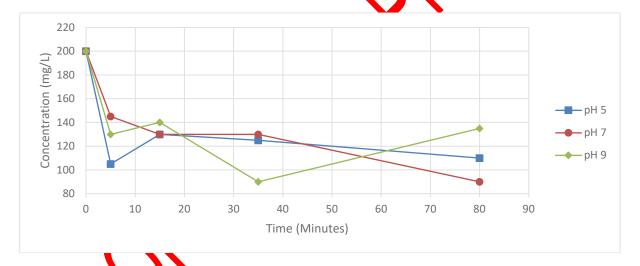


Figure 2. Concentration of MgCl₂ during the biochar activation

At a pH of 7, the concentration of magnesium sharply decreased during the first 5 minutes, then stabilized at around 130 mg/L between 20-40 minutes before gradually decreasing further to about 90 mg/L at the end of 80 minutes. The evidence indicates that neutral pH conditions provide a relatively stable retention phase followed by a gradual decline, suggesting effective ion exchange and cation adsorption over time compared to acidic (pH 5) or alkaline (pH 9) conditions[32].

These findings are consistent with existing literature on the impact of pH on biochar's ion exchange capacity. Jiang et al. [33] demonstrated that the adsorption kinetics of biochar are influenced by pH conditions, with neutral pH providing the ideal situation for cation exchange and nutrient retention. Meanwhile, Zhao et al. [46] discovered that acidic conditions (pH 5) do enhance the initial absorption of magnesium, however, the stability of adsorption decreases over time. Conversely, basic conditions (pH 9) also show high initial uptake but with lower retention compared to neutral pH. Hence, neutral pH can be considered as the optimal condition to maintain the stability of magnesium adsorption on biochar. These results suggest that biochar

activated at pH 7 offers the best balance of magnesium retention over time, making it the optimal condition for biochar's use in applications requiring long-term nutrient retention.

In summary, pH 7 is identified as the most effective condition for maintaining higher and more stable magnesium concentrations throughout the biochar activation process. The results highlight the importance of pH in optimizing biochar's nutrient retention capabilities, supporting the notion that neutral pH environments are most beneficial for maximizing magnesium adsorption and retention.

Nutrient Adsorption

The findings highlight the importance of optimizing contact time and biochar dosage to enhance the adsorption performance for ammonium and phosphate removal using biochar sourced from stabilization pond wastewater. The analysis examined the impact of these two factors on the outcomes of ammonium and phosphate adsorption rates and capacities in samples gathered from actual wastewater from a stabilization ponds. The changes in nutrient concentration during adsorption for ammonium and phosphate in four stabilization ponds are summarized in Figure 3. The figure highlights the reduction in concentration over contact time and variations among ponds.

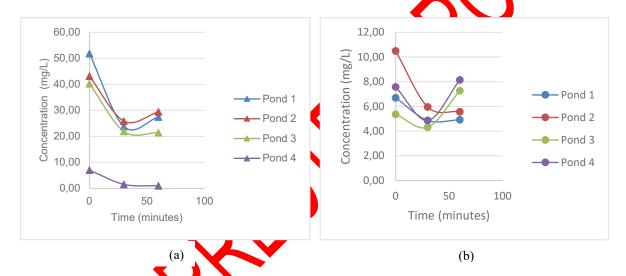


Figure 3. The nutrient concentration during the adsorption in wastewater: (a) Ammonium, (b) Phosphate

presents the changes in ammonium and phosphate concentrations during adsorption for the four stabilization pond samples. For ammonium, all ponds exhibit a sharp reduction within the first 30 minutes, followed by stabilization or a slight rebound at 60 minutes. Pond 1 and Pond 2 decline from above 40 mg/L to around 25 mg/L in the first 30 minutes, then increase slightly toward 60 minutes, while Pond 3 shows a similar pattern with only mind fluctuation. Pond 4 experiences the most significant decline, dropping from about 10 mg/L to nearly zero and remaining stable thereafter. These results confirm that biochar is highly effective in reducing ammonium levels during the initial contact period, with subsequent changes reflecting adsorption equilibrium. The linear regression results (R2 values) for ammonium adsorption further support the observation, showing relatively high values for most ponds, particularly Pond 1 ($R^2 = 0.6389$), which indicates a moderate correlation between time and ammonium reduction. For phosphate, the concentrations also decrease during the first 30 minutes across all ponds, with the most pronounced reduction observed in Pond 2 (from about 10 mg/L to 5 mg/L). However, phosphate levels tend to increase slightly after 30 minutes in most ponds, suggesting partial desorption or equilibrium adjustment during the later stage of the proces.

Similarly, phosphate adsorption also demonstrates a strong initial reduction in concentration during the first 30 minutes, followed by a plateau or slower decline after 60 minutes. The phosphate concentrations in the four ponds (Ponds 1, 2, 3, and 4) exhibit varying rates of decline, with Pond 1 showing a more pronounced reduction ($R^2 = 0.7687$). As such, like ammonium, phosphate is adsorbed more rapidly during the initial stages, with adsorption slowing as the biochar surface becomes saturated. These trend indicates that nutrients such as ammonium and phosphate are absorbed more rapidly in the initial stage due to the abundance sites available still the biochar Agusriyadin [47] explained that the acceleration in adsorption rate during the initial phase is a result of the high presence of pores and active surface area on the absorbing material. Meanwhile, Setyorini et al. [48] further explains that once the sites are filled, the rate of adsorption will decrease as the available absorption sites become limited. The phenomenon helps to clarify the pattern of rapid absorption rate at the beginning and then slowing down after reaching equilibrium. The decrease in adsorption speed following the initial phase is likely due to the active sites becoming saturated and a decrease in available unoccupied sites for additional adsorption.

The second set of graphs illustrates the effect of increasing biochar mass (0.5 grams) on ammonium and phosphate concentrations after 60 minutes of contact time. For both ammonium and phosphate, increasing the biochar dosage results in a more significant reduction in concentrations across all stabilization ponds. Pond 1 shows the most substantial reduction in nutrient concentrations, with ammonium concentrations dropping to less than 30 mg/L and phosphate concentrations nearing 5 mg/L at the highest brochar dosage. Ponds 2, 3, and 4 exhibit less dramatic reductions but still demonstrate improved adsorption with higher biochar masses.

Enhancing the quantity of biochar results in a greater ability to adsorb both ammonium and phosphate as it provides a larger surface area for ion exchange and adsorption to occur [49]. The higher mass of biochar provides more adsorption sites and promotes a higher rate of nutrient removal from the solution, which is confirmed by the data obtained in the research. Results indicate that biochar is an effective adsorbent for reducing nutrient concentrations in wastewater, with a greater biochar mass leading to enhanced nutrient removal. Ammonium is shown to be adsorbed faster and with better results than phosphate in the stabilization pond samples when comparing their adsorption rates. The accelerated removal of ammonium during the initial 30 minutes can be explained by its relatively small ionic size, enabling more efficient interaction with and adsorption onto the surface of the biochar. In the phosphate adsorption, being larger and more complex in structure exhibits slower adsorption kinetics. Such difference in adsorption rates can be explained by the distinct mechanisms of interaction between biochar and these two nutrients Wu & Vaneeckhaute [3], reported that ammonium is primarily absorbed through electrostatic forces and ion exchange mechanisms. Andreas [50], uncover that phosphate can interact with the surface of biochar through a complex surface complexation process that forms specific chemical bonds. Further, Krishna Murthy et al. [51] discovered that under certain conditions, phosphate can also undergo precipitation and electrostatic adsorption. The combination of these three mechanisms explains why phosphate has slower absorption kinetics compared to ammonium..

These findings are consistent with research by Gong [32] argued that the smaller ion radii and higher charge density allow ammonium ions to interact more quickly with the biochar surface. Jiang et al. [33] also stated that biochar is able to significantly reduce the concentration of ammonium and phosphate, but the efficiency of ammonium removal is much higher. Koulouri et al. [7] also discovered that increasing the biochar mass results in greater adsorption efficiency for both nutrients. Overall, these studies reinforce the findings of current investigation that ammonium is absorbed more quickly and effectively than phosphate in real wastewater. The increased biochar dosage provides more active sites for ion exchange and adsorption, which results in greater nutrient removal. The observed correlation between biochar

dosage and nutrient adsorption in present research supports these findings and emphasizes the importance of optimizing biochar mass for effective nutrient removal in wastewater treatment. Overall, the findings demonstrate that biochar effectively adsorb and lower levels of ammonium and phosphate in actual wastewater samples taken from stabilization ponds. The adsorption process is highly dependent on both contact time and biochar dosage, with ammonium being adsorbed more rapidly than phosphate. Increasing biochar dosage enhances the adsorption capacity for both nutrients, confirming that biochar is a viable method for nutrient removal from wastewater [52]. The findings herein are in line with literature and have confirmed biochar to be a promising sustainable technology for waste water treatment and nutrient recovery for environmental application.

Kinetic and Isotherm Analysis of the Nutrient Adsorption

Kinetic analysis allows for the exploration of the speed and processes associated with the absorption of ammonium and phosphate by biochar. By applying both first-order and second-order kinetic models to the experimental data for ammonium and phosphate adsorption, the dominant adsorption mechanism can be identified.

A kinetic and isothermal analysis is presented bellow to clarify the interactions between ammonium and phosphate and the biochar surface, as well as the mechanisms controlling nutrient sorption..

a) Ammonium Adsorption Kinetic

In samples taken from stabilization ponds, during the first 30 minutes of contact, the concentration of ammonium decreases rapidly before tapering off and reaching a steady state after 60 minutes. The information obtained from the study was evaluated using two different kinetic models. The results indicate that the second-order kinetics model provided a more accurate fit with higher R² value. Figure 4 displays the first-order and second-order kinetic reactions for ammonium uptake in wastewater samples from ponds 1 through 4 (P1-P4). The absorption rate in P3 shown the highest value with 0.21 mg/min, meanwhile the lowest was found in P1 with 0.03 mg/min. The data indicates that ammonium removal follows a chemisorption mechanism, with the chemical bonding between ammonium ions and the biochar surface controlling the reaction rate. These biochar materials commonly demonstrate second-order kinetic behaviour during ammonium adsorption because of their interactions with surface reactive groups and ion-exchange mechanisms.

Graphs in Figure 1 distrate the first-order and second-order kinetic plots for the removal of ammonium from wastewater samples in four ponds. The results depict appropriate quality and varying levels between the ponds.

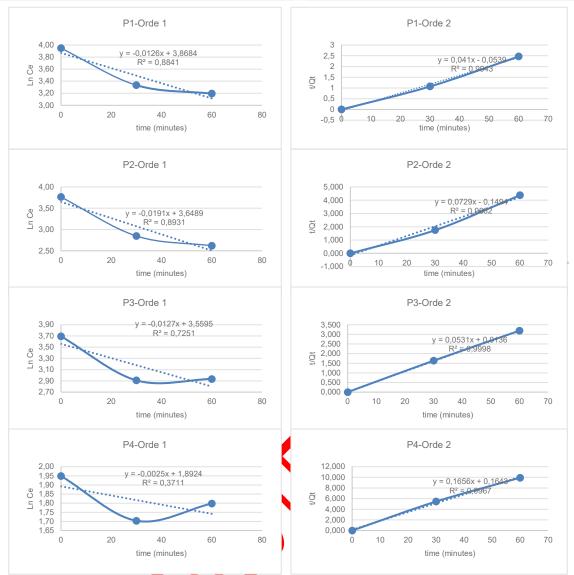


Figure 4. Reaction kinetics of first and second order for ammonium removal from wastewater across pond systems P1 to P4

After examining the kinetic performance for ammonium, the following section deliberates on phosphate adsorption to pinpoint differences in the rate and mechanism of adsorption.

b) Phosphate Adsorption Kinetic

During the process of phosphate adsorption, a decrease in concentration is noticed at the beginning, followed by a gradual slowing of the adsorption rate after 30 minutes, like attainmentation. The second-order model was found to be more accurate than the first-order model in predicting the adsorption process. The evidence suggests that the process of phosphate binding to biochar is similar to chemisorption, but occurs more slowly than with ammonium. The reason for the slowdown in phosphate absorption is because of its size being larger and the complex way it interacts with the surface of the biochar, which requires more time to form solid bonds [53]. The results emphasize that the absorption of ammonium and phosphate by biochar follows a second-order kinetic model, where chemical adsorption plays a key role in the removal process. Figure 5 displays the first order and second-order kinetic reactions for phosphate removal from wastewater samples across pond systems 1 through 4 (P1-P4). The phosphate absorption rate in P3 shown the highest value with 6.49 mg/minutes, meanwhile the lowest was found in P2 with 0.08 mg/minutes. The initial fast adsorption followed by a slower phase suggests that both ammonium and phosphate interact strongly with the biochar surface,

but phosphate requires more time to fully adsorb due to its larger size and different chemical behaviour.

The kinetic analysis of phosphate adsorption following first-order and second-order models is illustrated in <u>Figure 5</u>, indicating that adsorption follows pseudo-second-order behavior consistent with chemisorption.

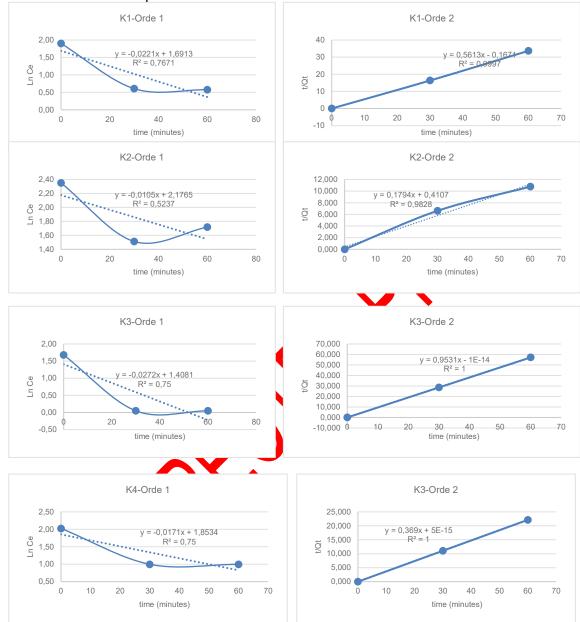


Figure 5. Reaction kinetics of first and second order for phosphate adsorption in the wastewater from pond 1 (P1) to pond 4 (P4)

After the kinetic evaluation, the research proceeded by analyzing the adsorption equilibrium behavior through isotherm modeling.

c) Ammonium Adsorption Isotherm

The Freundlich model demonstrated the highest level of accuracy for capturing ammonium adsorption, with an R² value up to 0.999. Result shows that the biochar surface contains a range of adsorption sites with different binding strengths. The Freundlich constant for ammonium suggesting a moderate capacity for adsorption where P1 has highest absorption capacity (24.39 mg/g) and P4 has lowest capacity with 6.04 mg/g. A n-value is less than 1, suggests that the

adsorption of ammonium is not highly favourable under the specific conditions of the present study. The observation corroborates the conclusions of Ren [54] who reported similar findings for ammonium adsorption on biochar, indicating that multiple adsorption sites are involved, but the adsorption efficiency could be improved with optimized biochar surface properties. The Langmuir model was less successful at fitting the ammonium adsorption data, with low R² values, indicating that ammonium adsorption on biochar does not follow monolayer adsorption [24]. Instead, the data implies that ammonium is attracted to various layers, showing that biochar's surface is diverse and has multiple binding sites for adsorption.

In order to complement the results of ammonium adsorption, the adsorption of phosphate was also analyzed using the same isotherm model for comparative evaluation.

d) Phosphate Adsorption Isotherm

The phosphate absorption is more in agreement with the Freundlich isotherm (R² × 0.98), suggesting that the absorption of phosphate on biochar is influenced by multiple absorption sites with varying energy levels. The Freundlich constant for phosphate absorption in 12 was 5.57 mg/g, which is lower than ammonium and the highest over the other ponds. Phosphate removal by biochar involves greater complexity and lower efficiency because of its larger ion dimensions [32] and the need for multiple binding locations to achieve effective attachment[55]. The Langmuir model did not accurately represent the phosphate absorption, indicating that phosphate may not adhere to just one layer on biochar but forms several layers during the adsorption process. The finidngs coincide with the conclusions drawn by other researchers. Likewise, the Freundlich model is commonly used to explain the adsorption of nutrients (such as ammonium and phosphate) on biochar [32], attributed to the diverse surfaces of biochar[56]. Furthermore, a better fit was obtained with the Freundlich isotherm than with the Langmuir model, indicating that the biochar surface is non-uniform and characterized by a diversity of adsorption site energies.

The research findings indicate that biochar can effectively decrease the levels of ammonium and phosphate in actual wastewater collected from stabilization ponds. The examination of kinetics revealed that the absorption of both nutrients follows second-order kinetics, suggesting that chemisorption significantly impacts the process. The adsorption behaviour of ammonium and phosphate ions on biochar surface is effectively explained by the Freundlich isotherm model, indicating the heterogeneous nature of the surface capable of adsorbing ions in various layers. According to the findings, biochar shows great potential as a substance for purifying wastewater [37], especially in the up taking nutrients[22]. However, enhancing biochar properties and boosting its ability to adsorb pollutants by modifying the surface or activating it could improve its effectiveness in environmental tasks like recovering nutrients and controlling pollution.

Ultimately, the rate and adsorption capacity are summarized to assess the overall performance of biochar adsorption under real wastewater conditions.

e) Adsorption Rate and Capacity

The adsorption capacity and rate for ammonium and phosphate were examinedusing biochar applied to real wastewater samples sourced from the stabilization ponds. The kinetics and adsorption isotherms provided valuable insights into the performance of biochar as an adsorbent for reducing nutrient levels in wastewater.

The adsorption capacity refers to the maximum amount of ammonium and phosphate that biochar can adsorb at equilibrium, and it is crucial for evaluating the efficiency of biochar in wastewater treatment. The results show that biochar exhibited varying adsorption capacities depending on the pond sample and the nutrient involved. The absorption capacity of magnesium-activated biochar for ammonium and phosphate in wastewater samples is summarized in **Table 1**.

Table 1. Adsorption capacity of biochar in wastewater

Pond	Ammonium Adsorption Capacity [mg/g]	Phosphate Adsorption Capacity [mg/g]
Pond 1	24.39	1.78
Pond 2	13.72	5.57
Pond 3	18.83	1.05
Pond 4	6.04	2.71

As seen from the <u>table 1</u>, among the sampled ponds, Pond 1 demonstrated the greatest ammonium adsorption capacity (24.39 mg/g), while Pond 3 recorded a moderately lower value of 18.83 mg/g. In contrast, Pond 4 has the lowest ammonium adsorption capacity at 6.04 mg/g. The highest phosphate adsorption capacity was also observed in Pond 2 (5.57 mg/g), whereas Pond 3 exhibited the lowest capacity for phosphate at 1.05 mg/g. These differences can be attributed to the varying biochar surface characteristics in each stabilization pond, as well as differences in the composition and characteristics of the wastewater from each pond, which can influence the availability of adsorption sites. Biochar with a higher surface area and more active sites tends to exhibit better adsorption capacities for nutrients like ammonium and phosphate [52].

The rate of adsorption signifies how quickly biochar adsorbs ammonium and phosphate. The adsorption rates for ammonium and phosphate were calculated based on the second-order model, and the reaction rate constants (k) are summarized in the following table. The constant of adsorption rate derived from the pseudo second-order kinetic model is presented in <u>Table 2</u>, indicating the variations in adsorption speed among different pond samples.

Table 2. Adsorption rate of biochar in wastewater

Pond	Ammonium Rate Constant	Phosphate Rate Constant
	[k, mg/min]	[k, mg/min]
Pond 1	0.03	1.89
Pond 2	0.04	0.08
Pond 3	021	6.49
Pond 4	0.17	0.91

Based on table 2, the adsorption rate for ammonium is relatively low across all ponds, with the highest rate constant observed in Pond 3 (0.21 mg/min), while Pond 1 has the lowest rate constant at 0.03 mg/min. In contrast, the phosphate adsorption rate varies more widely, with Pond 3 showing the highest phosphate rate constant (6.49 mg/min), suggesting that Pond 3 has a faster phosphate uptake rate compared to the other ponds. The evidence is consistent with the higher phosphate adsorption capacity observed in Pond 2, which has a significantly lower rate constant (0.08 mg/min) for phosphate adsorption. The adsorption rate constant (k) is a crucial parameter, as it indicates how quickly the adsorbent can remove contaminants from the solution. Higher values of (k) indicate faster adsorption processes.

These findings align with previous studies on the absorption capacity of biochar for ammonium and phosphate. Gong et al. [32] noted that the adsorption capacity of biochar for ammonium ranges from 5 to 30 mg/g, depending on the type of biochar and solution composition. Wijayanti & Kurniawati [45], discovered that the Freundlich isotherm model is the most appropriate for explaining nutrient adsorption in real wastewater because biochar surfaces are heterogeneous. Setyorini et al.[48] emphasizes that the heterogeneity creates variations in binding energy between adsorption sites that influence the absorption rate. The consistency of these findings suggests that the dominant mechanism in the adsorption process is chemisorption with Freundlich isotherm pattern. The experimental results demonstrate the

adsorption capacity and adsorption rate of biochar for reducing ammonium and phosphate concentrations in real wastewater from stabilization ponds. The findings suggest that biochar exhibits significant adsorption capacities, with Pond 1 showing the highest ammonium capacity and Pond 2 exhibiting the highest phosphate capacity. The adsorption rate constants confirm that biochar adsorption follows second-order kinetics, with Pond 3 showing the fastest adsorption for both contaminants.

The findings suggest that biochar has the potential to effectively remove nutrients from wastewater, and its effectiveness can be improved by adjusting the amount of adsorbent used and the duration of contact. Future studies should focus on improving the adsorption kinetics by modifying biochar properties to enhance the adsorption efficiency for both ammonium and phosphate, providing a sustainable solution for wastewater treatment and nutrient revery.

Scanning Electron Microscopy

The scanning electron microscope (SEM) was used to analyze the visual characteristics of biochar before and after activation, and after adsorping ammonium and phosphate from real wastewater samples. SEM pictures offer in-depth knowledge into the texture, porosity, and microstructure of biochar [13], which play a significant role in determining its ability to adsorb pollutants in water treatment processes [16].

The SEM analysis results indicated that biochar before activation process exhibited a relatively rough and irregular surface with imperfectly opened pores and fragmented materials. The condition rendered the biochar appearing smoother and less porous compared to activated biochar, thus reducing the number of active sites for adsorption as well. These findings are aligned with previous studies which reported that non-activated biochar had limitations in functional groups and underdeveloped pore structures, resulting in low effectiveness in removing pollutants such as ammonium and phosphate. The minimal presence of micro and macropores further reinforced the indication that non-activated biochar is less efficient in absorbing nutrients from wastewater [57].

After activation process with magnesium, the biochar surface undergoes significant changes manifested by an increase in pore size, rougher texture, and an increase in small pores. The addition of magnesium is believed to play a role in expanding the surface area and enriching the presence of functional groups on biochar. These structural changes result in increased reactivity of biochar and enhance its ability to adsorb ammonium and phosphate ions more effectively. The enhancement of the external texture is a common trait of biochar that has been activated through various means, such as physical or chemical processes [39] that boost its porosity and the number of active sites available [58]. The SEM analysis results indicate that a rougher texture and larger pores are closely related to the increase in biochar adsorption capacity. Muscarella et al. [10], demonstrates that chemically activated zeolite has higher porosity, thereby enhancing its ability to absorb ammonium. Alsulaili et al. [13] suggested that a wide porous structure provides greater opportunities for ion exchange and contaminant binding on the surface of biochar. As such, morphological changes due to the activation process directly contribute to increased adsorption efficiency.

Figure 6 shows the SEM analysis of biochar after adsorption in real wastewater from stabilization ponds. The SEM images display a marked difference in the biochar structure after adsorption, with visible accumulation of adsorbates on the biochar surface. The pores appear to be partially blocked, and some adsorption sites seem to have been filled with the adsorbed nutrients, further demonstrating the biochar's effectiveness in removing ammonium and phosphate from the wastewater. The surface change is indicative of adsorption saturation, where the biochar surface has been partially occupied by ammonium and phosphate ions. The partial blockage of pores and the presence of adsorbed material suggest that the biochar has effectively captured these contaminants [33]. The changes in biochar morphology after

adsorbing ammonium and phosphate from wastewater are clearly shown in <u>Figure 6</u>. The SEM image clearly illustrates the surface roughness, pore blockage, and adsorbate accumulation.

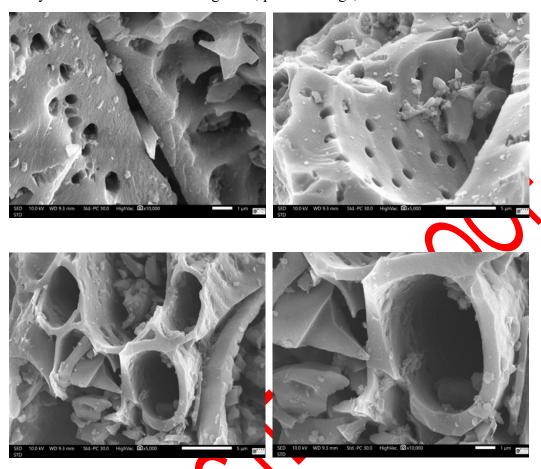


Figure 6. Biochar after adsorption

The reuse of treated wastewater from temples enriched with ammonium and phosphate has significant socio-economic potential in tropical regions such as Bali. The recovered nutrients can be transformed into affordable biochar fertilizers, reducing dependence on chemical fertilizers, supporting small-scale farmers, and strengthening circular economy practices based on local wisdom. From a policy perspective, the implementation of such technology can be facilitated through decentralized processing regulations, fiscal incentives, or public-private partnerships. The initiative aligns with the Sustainable Development Goals (SDGs), particularly SDG 6 11, and 12, and is relevant for South Asian regions with significant potential for utilizing temple waste to support community economic resilience and environmental protection.

CONCLUSION(S)

The findings confirm that magnesium-activated biochar derived from temple waste is an effective and sustainable adsorbent for recovering ammonium and phosphate from wastewater. Adsorption kinetics conformed to the pseudo-second-order model, indicating chemisorption dominance, while equilibrium data were best described by the Freundlich isotherm, reflecting surface heterogeneity and multilayer adsorption. Evaluation of multiple wastewater sources revealed variations in both adsorption capacity and rate, with the adsorption rate constant for phosphate reaching significantly higher values in certain samples, demonstrating the potential for rapid nutrient uptake under optimal conditions. These variations underline the importance of characterizing local wastewater and tailoring biochar application accordingly. The results

reinforces the feasibility of using locally sourced organic waste for nutrient recovery, contributing to environmental protection, resource circularity, and the development of cost-effective wastewater treatment solutions.

In addition to its technical performance, the findings emphasize the socioeconomic and policy dimensions of utilizing temple waste. The conversion of temple waste into activated magnesium biochar not only supports nutrient recovery, but also creates local economic value through the provision of affordable organic fertilizers, reducing costs for farmers, and strengthening cultural sustainability through circular economy practices based on local wisdom. Hence, policymakers in the South Asian region are encouraged to adopt a supportive regulatory framework, including incentives and community-based programs, to promote the adoption of biochar-based wastewater treatment technologies. The integration underscores the socioeconomic and cultural relevance of wastewater treatment, making it an essential component of sustainable resource management strategies in the region.

ACKNOWLEDGMENT(S)

The research was financially supported by the Kurita Water and Environment Foundation (KWEF) under the Kurita Overseas Research Grant (KORG) 2024, the Winistry of Higher Education, Science and Technology of the Republic of Indonesia, and Universitas Mahasaraswati Denpasar, which provided full support and facilitation.

Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

Author Contribution

The authors confirm contribution to the paper as follows: concept, study design, data analysis, manuscript draft: I Made Wahyu Wijaya; data collection, analysis data: I Made Wahyu Wijaya, I Ketut Sumantra, Ni Made Dharma Shantini Suena; analysis, interpretation of results, manuscript draft I Made Wahyu Wijaya, I Ketut Sumantra, Ni Made Dharma Shantini Suena Kailas Deoram Ahire, Pravin Mukund Nalawad. All authors reviewed the results and approved the final version of the manuscript.

Symbol		
q_e	Adsorption capacity	[mg/g]
C_0	Initial concentration of the adsorbate	[mg/L]
V	Volume of the solution	[L]
m	Mass of the biochar	[G]
q_t	Amount of adsorbate adsorbed at time tt	mg/g]
k	Rate constant	[mg/g·min or -]
t	Time of adsorption	[minutes
Ce	Equilibrium concentration of the adsorbate	[mg/L]
Qn	Maximum adsorption capacity	[mg/g]
K_{L}	Langmuir constant related to adsorption energy	[L/mg]]
K_{f}	Freundlich constant, adsorption capacity	[mg/g]
C_t	Concentration at time tt	[mg/L]
\mathbf{k}_1	Rate constant for first-order reaction	$[\min^{-1}]$
t_t	Time	[minutes]
n	Freundlich constant, adsorption intensity	-
NH_4^+ - N	Nutrient pollution from ammonium	-
PO_4^{3-}	Phosphate	-
$MgCl_2$	Magnesium chloride	-
NH_4^+	Ammonium	-

P1	Pond 1	-
P2	Pond 2	-
P3	Pond 3	-
P4	Pond 4	_

Abbreviation

RDF Refuse-Derived Fuel

SEM Scanning Electron Microscopy
EDTA Ethylenediaminetetraethanoic acid

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