Archives of Environmental Protection
Vol. 52 no. 2 pp. 27–38

PL ISSN 2083-4772
DOI: 10.24425/aep.2026.1292

Valorization of brewery wastewater sludge for phosphate removal: preparation, optimization, and performance of chemically activated carbon

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Keywords: kinetics, adsorption, pyrolysis, phosphate, wastewater sludge, chemical activation

Abstract: Phosphate discharge from industrial effluents, including brewery wastewater, contributes significantly to eutrophication and the degradation of aquatic ecosystems. The development of sustainable and low-cost materials for phosphate removal is therefore essential.

This study evaluates activated carbon produced from wastewater treatment sludge generated at Dashen Brewery (Gondar, Ethiopia) for phosphate removal from aqueous solutions. The sludge was chemically activated using phosphoric acid (H_3PO_4) and sodium hydroxide (NaOH), followed by thermal carbonization. Physicochemical characterization was performed using Brunauer–Emmett–Teller (BET) surface area analysis, Fourier transform infrared (FTIR) spectroscopy, point of zero charge (pHPZC), and proximate analysis. The H_3PO_4-activated carbon exhibited a well-developed porous structure with a surface area of 427.05 m^2/g and showed higher phosphate removal efficiency than the NaOH-activated samples. Optimization using response surface methodology (RSM-CCD) identified optimal conditions at pH 3, a contact time of 120 min, and an adsorbent dosage of 2.61 g/L, achieving 80.3% phosphate removal and an adsorption capacity of 13.6 mg/g. Adsorption kinetics followed a pseudo-second-order model, indicating chemisorption. Regeneration tests showed that the adsorbent retained over 50% of its initial efficiency after three cycles. The results demonstrate that brewery sludge can be effectively valorized into an efficient adsorbent for phosphate removal, with potential applicability to similar sludge streams from other breweries.

Introduction

The rapid expansion of industrial activities and increasing water demand have intensified pressure on aquatic environments, contributing to the deterioration of water quality (Filho et al., 2020). One of the major by-products of wastewater treatment processes is sewage sludge, which is generated in large quantities and poses significant disposal challenges due to the potential presence of heavy metals, pathogens, and other contaminants (Boualem et al., 2014). Among various water pollutants, phosphorus is a key contributor to aquatic ecosystem degradation. Excessive phosphorus discharge promotes eutrophication, resulting in oxygen depletion and deterioration of water quality. Major sources of phosphorus pollution include industrial effluents, mining activities, and agricultural runoff, making effective phosphate removal an urgent environmental priority (Yao et al., 2018).

Several technologies have been developed for phosphorus removal, including chemical precipitation, biological phosphorus removal, and adsorption. Chemical precipitation is often associated with high operational costs and the generation of secondary sludge, particularly at low phosphate concentrations. Biological phosphorus removal has attracted considerable attention; however, its efficiency may be limited by low influent phosphorus levels and operational constraints (Sarvajith & Nancharaiah, 2024; Mohamed et al., 2021; Lee et al., 2025; Mousazadeh et al., 2021). In contrast, adsorption has emerged as an efficient and flexible technique, especially suitable for low phosphate concentrations due to its simplicity and high removal efficiency (Yadav et al., 2021; Vaiškūnaitė et al., 2024; Sefatlhi et al., 2024).

Activated carbon is widely employed as an adsorbent owing to its high surface area, microporous structure, and strong affinity for a wide range of pollutants (Hammad et al., 2025; Wahidah et al., 2020; Michałek et al., 2025; Diyarova et al., 2025). However, the high cost of commercial activated carbon remains a significant limitation. Consequently,

increasing attention has been directed toward the development of low-cost activated carbons derived from industrial and agricultural wastes, offering both economic and environmental benefits through waste valorization (Sierra et al., 2023; Lv et al., 2023; Słomkiewicz et al., 2025).

Brewery wastewater treatment sludge represents a substantial solid waste stream generated during the treatment of brewery effluents. Improper management of this sludge can lead to secondary environmental pollution. Converting brewery sludge into activated carbon offers a viable strategy to address waste disposal challenges while producing a low-cost adsorbent. In particular, sludge generated at Dashen Brewery is abundant and readily available, making it a suitable precursor for value-added conversion.

In this context, the present study investigates the valorization of brewery wastewater treatment sludge through chemical activation and pyrolysis to produce activated carbon for phosphate removal. The influence of different activating agents (H_3PO_4 and NaOH) on adsorption performance was initially evaluated, and the most effective material was selected for further characterization and adsorption studies. In addition, the adsorption process was optimized using response surface methodology (RSM-CCD), and the regeneration performance of the adsorbent was also evaluated.

Materials and Methods

Sample collection and preparation

Mechanically dewatered sludge, the primary raw material used in this study, was collected from the wastewater treatment plant of Dashen Brewery, Gondar, Ethiopia (12°57′48″N, 37°43′43″E). Samples were collected at three-day intervals over a two-week period and thoroughly mixed to obtain a representative composite sample. The sampling campaign was conducted between 12 and 26 October 2024.

The composite sludge was initially sun-dried for 24 h (average temperature 28–32 °C) to reduce moisture content and odor, followed by manual removal of visible foreign materials. The sludge was then oven-dried at 105 °C for 24 h to ensure complete moisture removal.

After cooling in a desiccator, the dried sludge was ground using a disk mill and sieved to obtain particles in the size range of 2.8–3.5 mm (average size 3.15 mm). Particle size distribution was determined by sieve analysis. All sample preparation and analyses were conducted in triplicate to ensure reproducibility.

Chemical activation and carbonization process

The preparation of activated carbon from Dashen Brewery wastewater treatment sludge was carried out using both conventional pyrolysis (thermal activation only) and chemical activation, followed by pyrolysis, according to the procedure described by Filho et al. (2020).

Conventional pyrolysis

Approximately 50 g of sludge precursor (particle size 2.8–3.5 mm) was placed in a tubular reactor of a protein digester equipped with a nitrogen gas inlet and a temperature and heating rate control unit. The sample was pyrolyzed at 400 °C for 2 h under a continuous nitrogen flow without any chemical activation.

Chemical activation followed by pyrolysis

A 50 g portion of prepared sludge was transferred into separate 1 L cylindrical beakers containing phosphoric acid (H_3PO_4) or sodium hydroxide (NaOH) solutions at concentrations of 1, 2, and 3 M. The suspensions were stirred using a magnetic stirrer to ensure uniform impregnation and then left to stand for 4 h to promote the development of surface area and porosity. After impregnation, the solid and liquid phases were separated using Whatman filter paper (320 mm diameter). The solid fraction was oven-dried at 105 °C for 24 h to remove residual moisture (Al Dawery et al., 2023). The impregnated samples were then placed in heat-resistant cylindrical glass tubes and carbonized in a protein digester at 400 °C for 2 h under a continuous nitrogen flow (200 mL/min) with a heating rate of 10 °C/min (Filho et al., 2020; Streit et al., 2019; Yadav et al., 2021). After cooling in a desiccator, the NaOH- and H_3PO_4-activated carbons were washed with 1 M HCl and 1 M NaOH, respectively, to remove residual activating agents. The samples were subsequently rinsed with distilled water until neutral pH was achieved, then ground and sieved to obtain particle sizes of 2.2–2.8 mm for further use (Yadav et al., 2021).

Phosphate adsorption performance was evaluated in batch experiments. Approximately 3 g of activated carbon was added to 1 L of wastewater treatment effluent containing 40.4 mg/L phosphate at pH 5 and stirred for 60 min. After filtration, the residual phosphate concentration was determined using a photometer with Phosphate HR tablets.

Characterization of raw sludge and activated carbon

The proximate composition of raw sludge and activated carbon (moisture, ash, volatile matter, and fixed carbon) was determined according to ASTM standard methods (ASTM, 2004).

The specific surface area was measured using a NOVA Instruments analyzer based on multilayer nitrogen adsorption. Approximately 0.5 g of each sample was degassed at 300 °C for 3 h under vacuum prior to analysis. Nitrogen adsorption–desorption measurements were conducted at atmospheric pressure, and the surface area was calculated using the Brunauer-Emmett-Teller (BET) method (Kassahun et al., 2022).

FTIR spectra of raw sludge and activated carbon were recorded in the range of 400–4000 cm^{-1} using a JASCO FT/IR-6600 spectrometer to identify functional groups and chemical bonds (Yao et al., 2018).

The point of zero charge (pHPZC) was determined using the solid addition method. Activated carbon (0.5 g) was added to solutions with initial pH values from 2 to 10 and shaken for 24 h. The pHPZC was identified from the intersection of ΔpH (pH_final − pH_initial) with the x-axis (Mousazadeh et al., 2021).

Experimental procedure for phosphate removal

Batch adsorption experiments were performed using wastewater with an initial phosphate concentration of 40.8 mg/L. The effects of contact time, pH, adsorbent dosage, and initial phosphate concentration were investigated. Preliminary one-variable-at-a-time experiments were conducted to establish suitable parameter ranges. A full factorial design (3 × 3) with

Table 1: Factors and levels for the phosphate removal experiment

Factor	Minimum level	Intermediate level	Maximum level
Dosage (g/L)	1	2	3
PH	3	6.5	10
Contact time (min.)	60	90	120

two replicates was employed to assess the combined effects of adsorbent dosage, pH, and contact time (Table 1).

For each run, 1000 mL of wastewater was placed in a 1 L beaker and stirred at 120 rpm. The pH was adjusted using 1 M HCl or 1 M NaOH and monitored with a digital pH meter at room temperature. After the adsorption period, the suspension was allowed to settle for 2 min and then filtered using Whatman filter paper.

Phosphate concentrations before and after adsorption were measured using a Palintest™ 8000 photometer with a Phosphate HR test kit. A 10 mL sample was reacted with one HR tablet, allowed to develop color for 10 min, and analyzed according to the manufacturer's protocol.

Phosphate removal efficiency (R, %) was calculated using Equation (1):

$$R = (C_0 - C\_f) / C_0 \times 100 \quad (1)$$

where C_0 and C_f are the initial and final phosphate concentrations (mg/L), respectively. All experiments were conducted in duplicate.

Experimental design and data analysis

The experiment was designed to evaluate the individual and interaction effects of adsorbent dose, pH, and contact time on phosphate removal efficiency using response surface methodology (RSM). RSM was applied to model the relationships between process variables and the response and to optimize the operating conditions (Sureshkumar & Susmita, 2018).

A central composite design (CCD) was employed due to its suitability for fitting quadratic models while reducing the number of experimental runs and enabling interaction analysis (Dhahri et al., 2022). The CCD consisted of 8 factorial points, 6 axial points, and 6 center-point replicates, resulting in 20 experimental runs.

Data analysis was carried out using Design-Expert software (version 13.0.5). The coded and actual levels of the variables are presented in Table 2. All batch adsorption experiments were performed as single runs for each experimental condition, while experimental error was estimated from the replicated center points included in the CCD.

Statistical modelling of the activated carbon production process

The experimental data were fitted to a quadratic regression model (Equation 2), incorporating three linear terms, three interaction terms, three quadratic terms, and an intercept:

$$Y = X_0 + X_1A + X_2B + X_3C + X_4AB + X_5AC + \\ + X_7A^2 + X_8B^2 + X_9C^2 \quad (2)$$

Where: Y is the response variable; X_0 is the intercept; $X_1 - X_3$ are the linear coefficients; $X_4 - X_6$ are the interaction coefficients; and $X_7 - X_9$ are the quadratic coefficients. A, B, and C represent the coded levels of the independent variables (contact time, adsorbent dose, and pH, respectively) (Latinwo et al., 2019).

Model adequacy and significance were evaluated using analysis of variance (ANOVA) and the coefficient of determination (R^2). Numerical optimization based on the RSM-CCD approach was applied to identify operating conditions that maximized phosphate removal efficiency. The optimized conditions were validated through duplicate experiments conducted within the predefined experimental range.

Adsorption Isotherms and Kinetics Models

Adsorption isotherms were studied by varying the adsorbent dosage (0.5–3.0 g/L) at pH 3, contact time of 120 min, and keeping other parameters constant based on prior phosphate removal results. The adsorption capacity (q_e, mg/g) as a function of the equilibrium solute concentration (C_e, mg/L) at constant temperature defines the isotherm. The Langmuir and Freundlich models, widely used in the literature, were applied to analyze the adsorption behavior (Filho et al., 2020).

Table 2: Combination of parameters for batch adsorption experiments

	Factor 1	Factor 2	Factor 3
Run	A: contact time, min	B: dose, g	C: pH
1	120	3	3
2	60	3	3
3	60	1	10
4	120	1	3
5	120	1	10
6	60	1	3
7	140	2	6.5
8	90	2	12
9	90	2	6.5
10	90	2	6.5
11	90	2	6.5
12	90	2	6.5
13	90	2	6.5
14	120	3	10
15	90	4	6.5
16	60	3	10
17	90	0.3	6.5
18	40	2	6.5
19	90	2	6.5
20	90	2	0.6

Freundlich Isotherm

The Freundlich isotherm is an empirical model expressed as:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (3)$$

Where: q_e is the amount of solute adsorbed per unit mass of adsorbent (mg/g); C_e is the equilibrium solute concentration (mg/L); K_f is the Freundlich adsorption capacity constant; and $1/n$ is the adsorption intensity parameter.

Langmuir Isotherm

The Langmuir isotherm assumes monolayer adsorption on a homogeneous surface and is represented as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m}\cdot\frac{1}{C_e} \quad (4)$$

Where: q_m is the maximum adsorption capacity (mg/g); K_L is the Langmuir adsorption constant (L/mg); and C_e is the equilibrium solute concentration (mg/L).

Kinetics of adsorption

Adsorption kinetics were studied at pH 3 using a fixed adsorbent dose of 3 g/L, with continuous stirring at 120 rpm at room temperature. Phosphate removal was monitored at 60, 80, 100, and 120 min. Equilibrium was considered to be reached when no significant change in adsorption capacity was observed (Mohammad et al., 2014). The experimental data were fitted to pseudo-first order and pseudo-second-order kinetic models to determine the adsorption mechanism and corresponding rate constants.

Pseudo-first-order model

The pseudo-first-order kinetic model is expressed as:

$$\log(q_e - q_c) = \log q_e - \frac{k_1}{2.303}t \quad (5)$$

Where: q_e is adsorption capacity at equilibrium (mg/g); q_t is adsorption capacity at time t (mg/g); k_1 is pseudo-first-order rate constant (min^{-1}).

A plot of log ($q_e - q_t$) versus t is expected to be linear, from which k_1 and q_e can be determined from the slope and intercept, respectively.

Pseudo-second-order model

The pseudo-second-order kinetic model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Where: q_e is adsorption capacity at equilibrium (mg/g); q_t is adsorption capacity at time t (mg/g); k_2 is pseudo-second-order rate constant (g/mg·min).

A plot of t/q_t versus t is expected to be linear, from which q_e and k_2 can be calculated from the slope and intercept, respectively.

Regeneration of sludge-based activated carbon

Chemical regeneration, which preserves the adsorbent's pore structure, was used to evaluate the reusability of sludge-based activated carbon (Dhahri et al., 2022). For each cycle, 3 g of adsorbent was added to 500 mL of 80.4 mg/L phosphate solution at pH 3 and stirred at 120 rpm for 90 min. Desorption was then performed using 500 mL of 0.1 M NaOH, with shaking for 12 h, followed by centrifugation and repeated washing with distilled water until neutral pH was reached. The adsorption–desorption cycle was repeated five times, and phosphate concentrations in the supernatant were measured after each cycle to assess reusability.

Results and Discussion

Characterization of raw sludge and activated carbon

Three materials were produced during the study: conventional carbon obtained by pyrolysis, NaOH-activated carbon, and H_3PO_4-activated carbon. Preliminary adsorption tests were carried out to compare their phosphate removal performance. Since the H_3PO_4-activated carbon exhibited superior adsorption efficiency, detailed physicochemical characterization was focused on this material.

Proximate analysis

Proximate analysis was used to determine the volatile matter, moisture, ash, and fixed carbon contents of raw sludge and activated carbon (Table 3). Activation significantly improved the physicochemical properties of the material: the activated carbon showed higher fixed carbon, lower moisture content, and reduced ash content compared with raw sludge. These changes result from thermal and chemical activation processes, which break down the sludge molecular matrix and increase the relative carbon fraction (Kassahun et al., 2022).

The observed changes in proximate composition are consistent with the structural transformation of sludge during chemical activation and pyrolysis. The increase in fixed carbon content and the reduction in volatile matter indicate the formation of a more stable carbon matrix. Chemical activation promotes the removal of non-carbon components and enhances pore development, thereby improving adsorption performance.

Point of zero charge (pHPZC) analysis

The adsorption of phosphate ions is strongly influenced by the surface charge of the activated carbon, which depends on solution pH. The point of zero charge (pHPZC) is defined as the pH at which the net surface charge is zero (Dhahri et al., 2022), determined from the intersection of ΔpH (pH_final – pH_initial) versus initial pH with ΔpH = 0. Below the pHPZC, the surface is positively charged, favoring electrostatic attraction of negatively charged phosphate ions; above the pHPZC, the surface becomes negatively charged, reducing adsorption efficiency. The pHPZC of the activated sludge-based carbon was 6.5 (Figure 1), indicating that favorable phosphate adsorption occurs at pH < 6.5. This value also reflects the influence of the activation process on surface

Table 3: Proximate analysis results of raw and activated sludge

No	Parameter	Raw sludge, %	Activated carbon, %
1	Moisture content	12.80	5.20
2	Ash content	14.00	18.64
3	Volatile mater	28.32	15.18
4	Fixed carbon	37.52	48.37

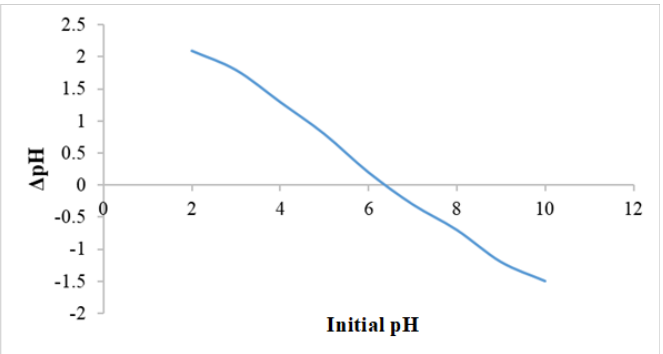

Fig. 1. Determination of the point of zero charge (pHPZC) of the sludge-based activated carbon.

chemistry of the adsorbent. Chemical activation, particularly with H_3PO_4, introduces oxygen-containing functional groups and modifies surface charge properties, enhancing electrostatic interactions with negatively charged phosphate species. These surface modifications play an important role in determining the adsorption efficiency of the produced activated carbon.

Brunauer–Emmett–Teller (BET) surface area analysis

Based on the preliminary adsorption results, the H_3PO_4-activated carbon exhibited superior phosphate removal performance compared with NaOH-activated carbon. Therefore, detailed physicochemical characterization, including BET surface area analysis, was conducted for the H_3PO_4-activated sample, selected as the most promising adsorbent.

Surface area is a key parameter influencing adsorption efficiency, as it determines the number of accessible active sites available for adsorbate molecules. BET analysis showed that the specific surface area increased from 80.57 m^2/g for raw sludge to 427.05 m^2/g after activation, indicating substantial pore development induced by chemical activation with H_3PO_4 and thermal treatment. For comparison, black liquor sludge-based activated carbon (AC) exhibited a surface area of 302.5 m^2/g (Wahidah et al., 2020), while activated carbons produced under various conditions ranged from 400–700 m^2/g (Kassahun et al., 2022) and 124–1433 m^2/g for agricultural waste-derived carbons (De Gisi et al., 2016), which is consistent with values reported for sludge-derived adsorbents in the literature (Vaiškūnaitė et al., 2024; Filho et al., 2020). These results confirm that the applied activation method effectively enhanced surface area, making the sludge-based AC comparable to other waste-derived activated carbons. Similar approaches using wastewater sludge as a precursor for activated carbon production have also been reported in the literature, demonstrating promising adsorption performance for various pollutants (Filho et al., 2020; Filho et al., 2021; Filho et al., 2023).

FTIR Spectra Analysis

Fourier-transform infrared (FTIR) spectroscopy was used to identify functional groups in the wastewater sludge before and after activation. The spectra revealed peaks corresponding to –OH, C–H, C=O, N–H, and C–O groups, reflecting the chemical complexity of the adsorbent and its potential for phosphate adsorption.

As shown in Figure 2, the broad peak at 3250 cm^{-1} corresponds to hydrogen-bonded –OH groups from alcohols and carboxylic acids (Latinwo et al., 2019), while the peak at 2884 cm^{-1} is attributed to C–H stretching in alkanes. The band at 1755 cm^{-1} is assigned to C=O stretching vibrations, likely associated with esters or carbonyl groups formed during activation. The peak at 1508 cm^{-1} indicates aromatic C=C stretching or N–H bending from amine groups (Mohamed et al., 2023), while the peak at 1040 cm^{-1} corresponds to C–O stretching. The band at 498 cm^{-1} reflects phosphate groups, likely introduced by H_3PO_4 activation.

Comparison of spectra before and after activation shows shifts in N–H, C=C, C–O, and C–H peaks, suggesting the involvement of these functional groups in phosphate adsorption. These shifts also indicate changes in the chemical environment resulting from thermal and chemical activation, as well as increased surface area development (Almahbashi et al., 2021; Kassahun et al., 2022).

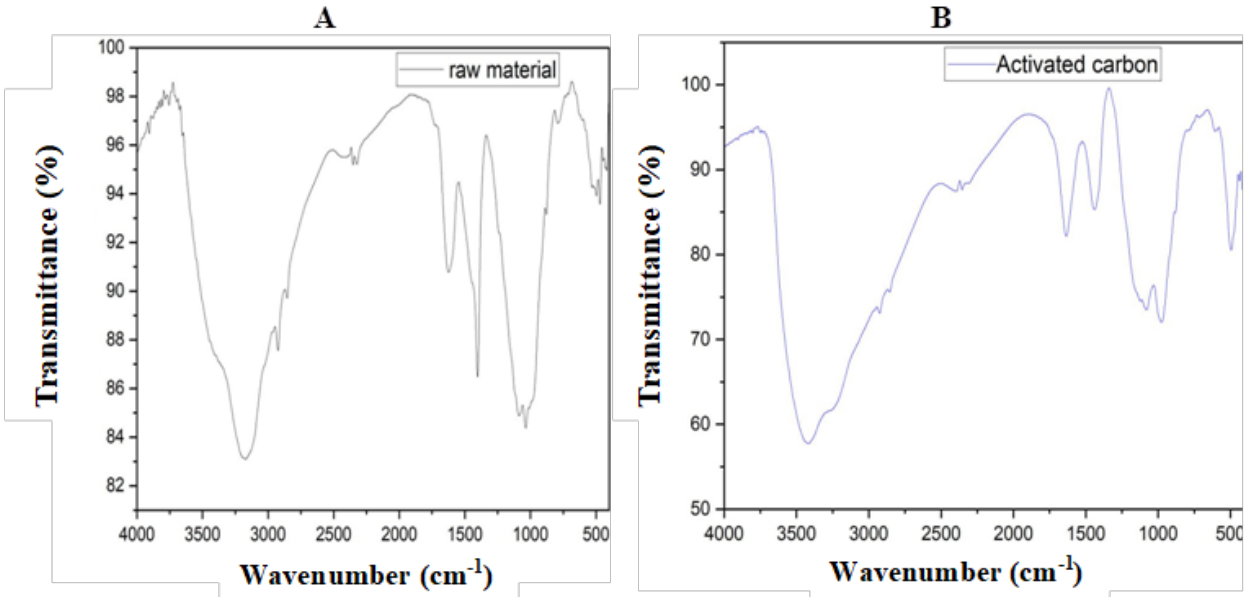

Fig. 2. FTIR spectra of raw sludge and H_3PO_4 - activated carbon.

Table 4: Result of phosphate removal efficiency at different chemical concentration

Run	Activating Agent	Concentration	Removal Efficiency %	Adsorption Capacity mg/g
1	NaOH	1	52.6	2.56
2	NaOH	2	58.3	5.21
3	NaOH	3	58.5	4.39
4	H_3PO_4	1	68.32	7.58
5	H_3PO_4	2	73.52	9.2
6	H_3PO_4	3	74.5	13.6
7	Conventional pyrolysis activation	-	33.5	3.33

Wastewater Sludge Activated Carbon

The activation process was performed to enhance the surface area, porosity, and adsorption affinity of the wastewater sludge. The phosphate removal performance of the produced sludge-based activated carbon was evaluated in terms of removal efficiency and adsorption capacity. Table 4 summarizes the phosphate removal efficiency of activated carbon prepared using different concentrations of NaOH and H_3PO_4, as well as without chemical activation (conventional pyrolysis). The chemical–sludge contact time was maintained at 60 min.

The results indicate that phosphate removal efficiency increased with increasing activator concentration, ranging from 52.6% to 74.5%. Activated carbon produced via chemical activation followed by pyrolysis exhibited significantly higher removal efficiency than carbon obtained by pyrolysis alone (33.5%). Among the activating agents, H_3PO_4-activated sludge outperformed NaOH-activated sludge at equivalent concentrations, with the highest removal efficiency (74.5%) and adsorption capacity (13.6 mg/g) achieved using 3 M H_3PO_4.

Based on these preliminary results, H_3PO_4-activated carbon was selected as the most promising material and used for further physicochemical characterization (BET, FTIR, and pHPZC) and detailed adsorption studies.

The superior performance of H_3PO_4-activated carbon can be attributed to its activation mechanism. Phosphoric acid promotes bond cleavage within the sludge matrix, facilitating the release of volatile components and the formation of a well-developed porous structure (Neme et al., 2022), which enhances pore development and adsorption performance, as also reported for chemically activated biochars (Sefatlhi et al., 2024; Lv et al., 2023). This enhanced porosity increases

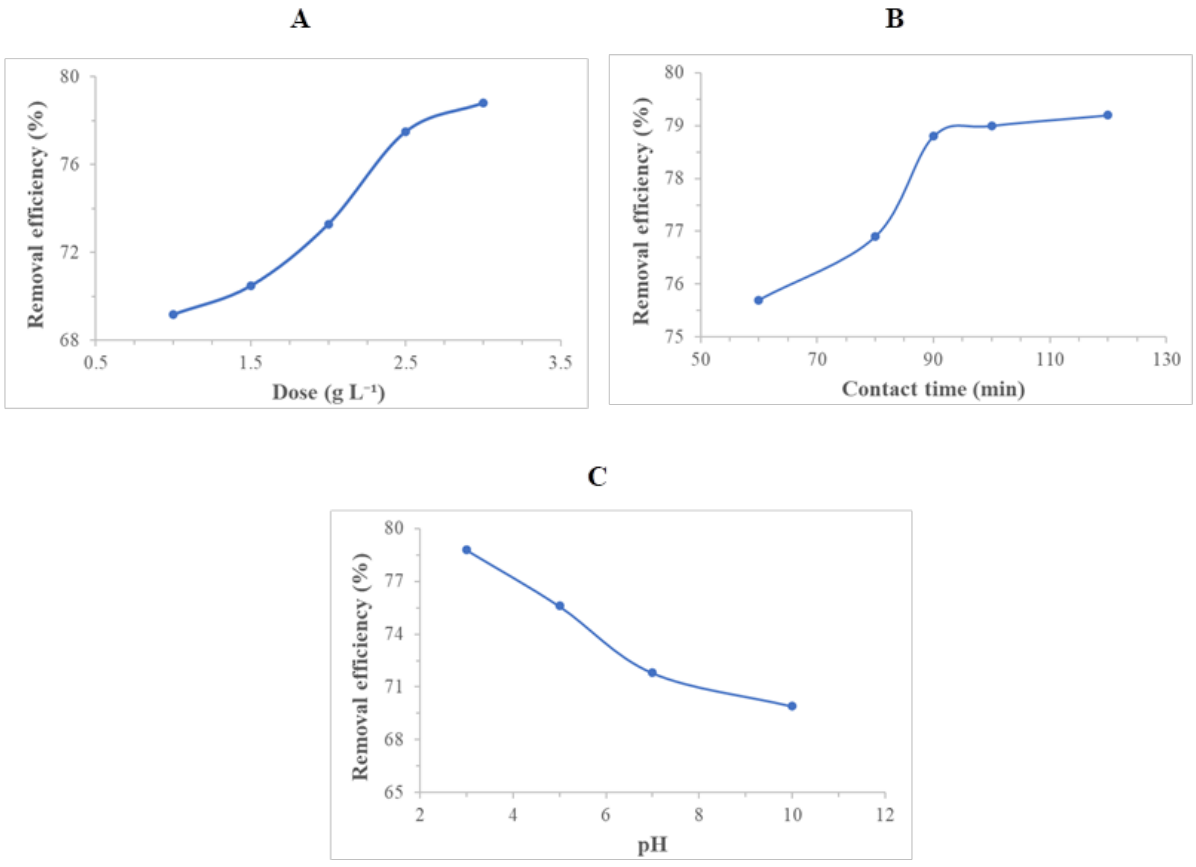

Fig. 3. Effect of operating parameters on phosphate removal efficiency: (A) adsorbent dose, (B) contact time, and (C) solution pH.

the availability of active sites for phosphate adsorption. For comparison, similar adsorption capacities have been reported in the literature, for example, 12.39 mg/g for phenol adsorption onto rice husk-derived activated carbon (Mohammad et al., 2014), which is comparable to the 13.6 mg/g observed here for phosphate. Phosphoric acid activation is widely recognized as an effective method for developing porous carbon structures and enhancing adsorption performance, as reported in previous studies on biomass-derived adsorbents (Da Silva et al., 2023).

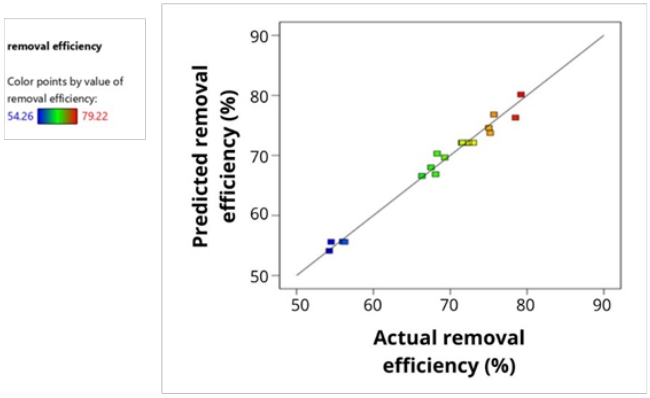

Fig. 4. Predicted versus actual values of phosphate removal efficiency obtained from the response surface model.

Effects of Individual Adsorption Process Parameters

The effects of key operational parameters on phosphate adsorption were examined using a one-variable-at-a-time approach, in which each factor was varied while the others were kept constant.

Effect of adsorbent dose

The influence of adsorbent dose on phosphate removal at a fixed contact time (90 min) and pH 3 is shown in Figure 3A. Increasing the dose from 1 to 2.5 g/L enhanced removal efficiency from 69.3% to 77.5%, while a further increase to 3 g/L resulted in only marginal improvement. At lower doses, the number of available adsorption sites is limited. Increasing the dose provides more active sites and greater surface area; however, beyond a certain level, additional adsorbent does not significantly improve removal efficiency due to site saturation (Yao et al., 2018).

Effect of contact time

As shown in Figure 3B, phosphate removal increased from 75% to 79% as contact time was extended from 60 to 90 min at an adsorbent dose of 3 g/L and pH 3. Further increases in contact time did not substantially improve adsorption, indicating that equilibrium had been reached. The initial rapid uptake phase is attributed to the availability of abundant active sites, whereas the subsequent slower phase is controlled by phosphate transport into the adsorbent and repulsion among already adsorbed molecules (Kassahun et al., 2022).

Effect of solution pH

Figure 3C illustrates the effect of solution pH on phosphate removal at an adsorbent does of 3 g/L and a contact time of 90 min. Removal efficiency decreased from 79% at pH 3 to 71.5% at pH 6.5 and 68% at pH 10. At low pH, the positively charged adsorbent surface attracts negatively charged phosphate ions.

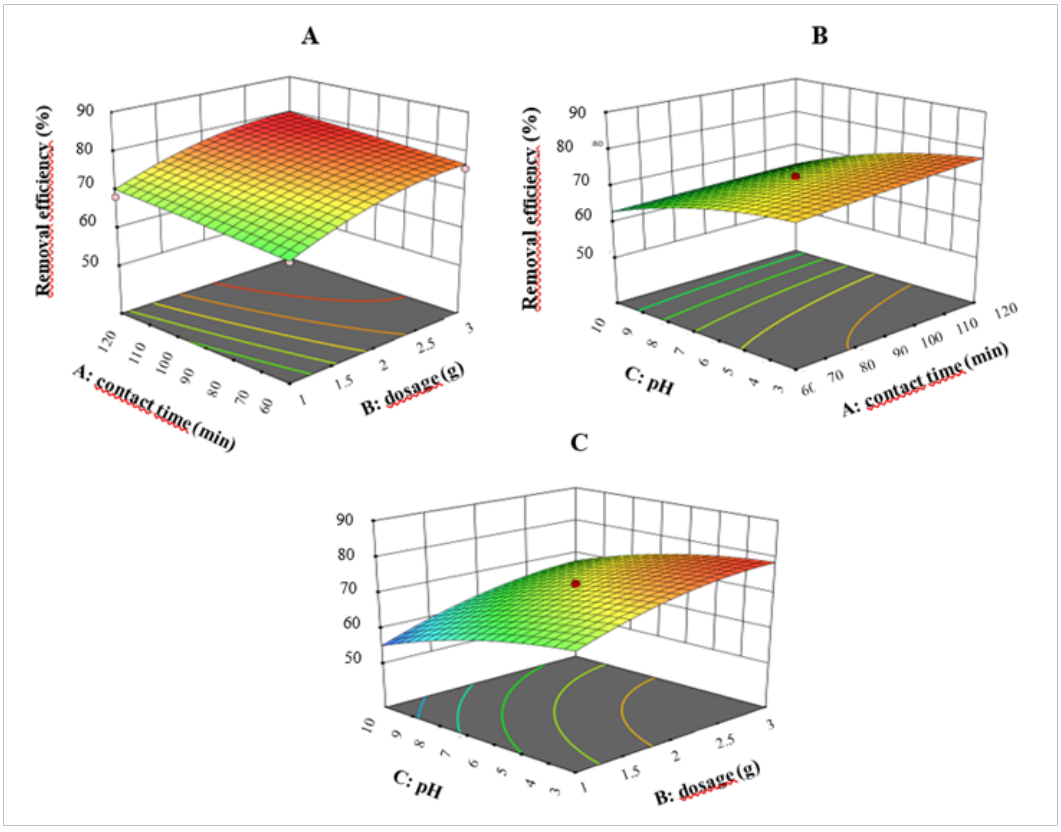

Fig. 5. Three-dimensional response surface plots showing the interaction effects of (A) adsorbent dose and contact time, (B) pH and contact time, and (C) pH and adsorbent dose on phosphate removal efficiency.

Table 5: Summary of isotherm, kinetics constants and R^2 values

Model	**Langmuir isotherm**			**Freundlich isotherm**		
Constant	$q_{m,}$ mg/mg	$K_{L,}$ L/mg	R^2	Kf, mg/g	1/n	R^2
Value	10.13	1.08	0.981	1.3867	0.1897	0.9364
Model	**pseudo-first-order**			**second-order**		
Constant	$q_{e,}$ mg/mg	$K_{1,}$ min^{-1}	R^2	$q_{e,}$ mg/mg	K_2(g/mg)min^{-1}	R^2
Value	10.13	1.08	0.9257	1.3867	0.1897	0.9915

Above the pHPZC (6.5), the surface becomes negatively charged, causing electrostatic repulsion and reduced adsorption efficiency.

Interaction Effects of Process Variables on Phosphate Adsorption

The interaction of contact time (A), adsorbent dose (B), and solution pH (C) on phosphate removal by sludge-based activated carbon was evaluated using response surface methodology (RSM). A statistically significant quadratic model ($p < 0.0001$) with a high coefficient of determination ($R^2 = 0.9837$) accurately described the system. ANOVA confirmed the significance of the model and the contributions of the individual factors. Six duplicate midpoint experiments were performed to ensure reproducibility and assess experimental error.

The empirical quadratic model relating phosphate removal efficiency (RE, %) to the process variables is:

$$RE = 72.13 + 1.22 \cdot A + 5.65 \cdot B - 6.15 \cdot C - 0.15 \cdot \cdot A^2 - 2.49 \cdot B^2 - 2.19 \cdot C^2 - 0.0975 \cdot (A \cdot B) - 0.5475 \cdot \cdot (A \cdot C) + 0.6325 (B \cdot C) \quad (7)$$

where A is contact time (min), B is adsorbent dose (g/L), and C is solution pH.

Figure 4 shows the predicted versus experimental RE values, with minimal deviation from the diagonal line, indicating that the model reliably captures the interactions among the three variables.

Combined Effects of Process Variables

The combined effects of contact time, adsorbent dose, and solution pH on phosphate removal are illustrated in Figure 5A–C. Removal efficiency increased from 54.3% to 78.5% as contact time and adsorbent dose increased from 60 to 90 min and 1 to 2 g/L, respectively (Figure 5A). Further increases to

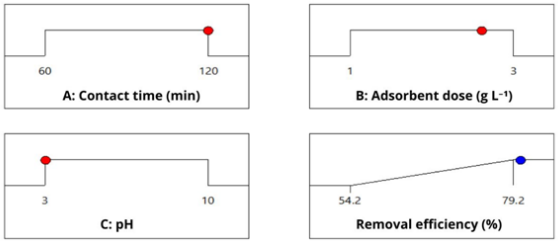

Fig. 6. Desirability function plot used to determine the optimal conditions for phosphate removal.

120 min and 3 g/L resulted in only a marginal improvement (up to 79.2%), indicating that adsorbent dose has a more pronounced effect than contact time. At a fixed adsorbent dose of 2 g/L, removal efficiency rose from 67% to 78.5% as contact time increased from 60 to 90 min and pH decreased from 10 to 3, gradually reaching 79.2% beyond these conditions (Figure 5B). This demonstrates that adsorption is directly proportional to contact time and inversely proportional to pH. Lower pH values enhance electrostatic attraction between the positively charged adsorbent surface and negatively charged phosphate ions.

Similarly, at a constant contact time of 90 min, phosphate removal increased from 58.4% to 78.4% as adsorbent dose increased from 1 to 3 g/L and pH decreased from 10 to 3 (Figure 5C). This indicates that higher adsorbent doses consistently improve phosphate removal across all pH levels, with acidic conditions favoring adsorption compared to neutral or basic media. Overall, these results highlight the synergistic effects of the process variables and emphasize the importance of optimizing adsorbent dose and solution pH to maximize phosphate removal efficiency.

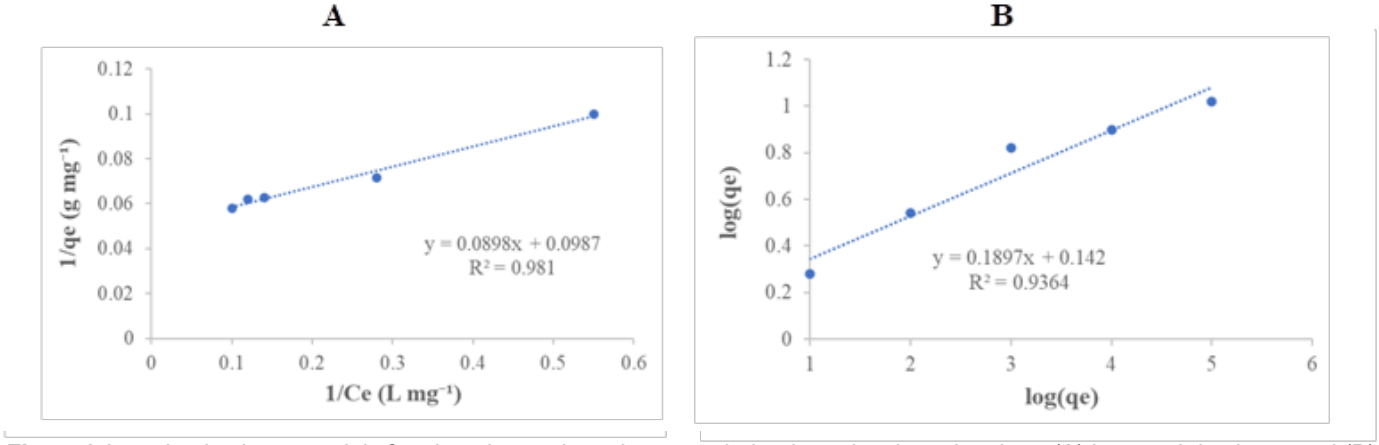

Fig. 7. Adsorption isotherm models for phosphate adsorption onto sludge-based activated carbon: (A) Langmuir isotherm and (B) Freundlich isotherm.

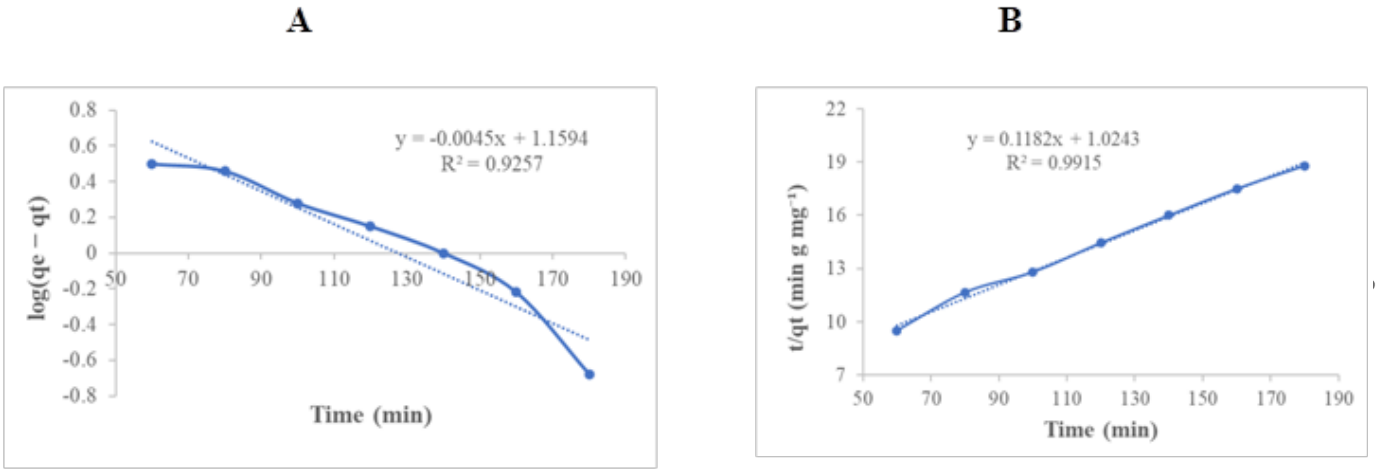

Fig. 8. Adsorption kinetic models for phosphate removal: (A) pseudo-first-order model and (B) pseudo-second-order model.

Response Optimization and Verification

The phosphate removal process using sludge-based activated carbon was optimized using removal efficiency as the response variable. Numerical optimization was performed using the desirability function in Design Expert 13.0.5, with adsorbent dose, contact time, and solution pH varied within the studied ranges to maximize phosphate removal (Fig. 6). The predicted optimum conditions were an adsorbent dose of 2.608 g/L, a contact time of 120 min, and pH 3, corresponding to a maximum predicted removal efficiency of 80.24%. Verification experiments conducted under these conditions yielded an average removal efficiency of 78.9%, with a percentage error of -1.70%, confirming the reliability of the model. The high desirability value of 0.941 indicates excellent agreement between predicted and experimental results. For comparison, Latinwo et al. (2019) reported a desirability value of 0.555 for phosphoric acid-activated flamboyant pod carbon, with a percentage error of -1.30%. The observed removal efficiency obtained in this study is comparable values reported in the literature: Ahmad et al. (2022) achieved 80% removal using activated bentonite, while Yapo et al. (2022) and Ahmad et al. (2023) reported efficiencies of 89% and 90.6%, respectively. These results confirm that sludge-based activated carbon is an effective and competitive adsorbent for phosphate removal from wastewater.

Adsorption Isotherm and Kinetics Analysis

Adsorption isotherms describe the relationship between the adsorbent's capacity and the equilibrium concentration of phosphate at constant temperature, providing insight into surface interactions. The experimental data were fitted to Langmuir and Freundlich models. Regression analysis yielded R^2 values of 0.981 for Langmuir and 0.9364 for Freundlich (Figure 7), with the corresponding constants summarized in Table 5. The higher R^2 for Langmuir model indicates monolayer adsorption on a homogeneous surface, where each site binds one phosphate molecule, consistent with a monolayer adsorption mechanism (Pedrosa et al., 2022).

Kinetic studies using pseudo-first-order and pseudo-second-order models showed R^2 = 0.9257 and R^2 = 0.9915, respectively (Figure 8). The higher R^2 for the pseudo-second-order model suggests that phosphate adsorption onto sludge-based activated carbon is governed by chemisorption, involving electron sharing or exchange between phosphate ions and the

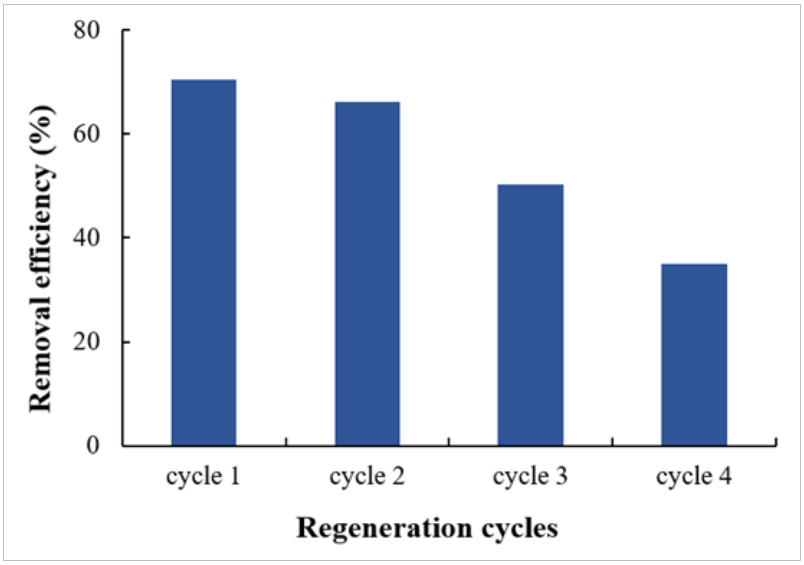

Fig. 9. Effect of regeneration cycles on phosphate removal efficiency of the sludge-based activated carbon.

adsorbent surface, which is consistent with previous studies on biochar-based adsorbents (Sefatlhi et al., 2024). The kinetic constants are presented in Table 5.

Regeneration Studies

The reusability of sludge-based activated carbon was evaluated over four adsorption–desorption cycles (Figure 9). Phosphate removal efficiency decreased from 70.5% in the first cycle to 35% in the fourth, with drops of 9% and 15.7% during the first and second cycles, respectively. The adsorbent maintained satisfactory performance up to the third cycle.

The decline in efficiency is attributed to two primary factors (Kassahun et al., 2022): (i) loss of adsorbent during recovery, which reduces available surface area and active sites, and (ii) changes in adsorbent properties, such as fouling or irreversible aggregation, which block adsorption sites. In addition, partial pore blockage by strongly bound phosphate species and gradual modification of surface functional groups during alkaline desorption may further contribute to the observed decrease in adsorption performance after repeated cycles. Despite these effects, the sludge-based activated carbon demonstrated satisfactory reusability for up to three cycles.

In summary, the findings confirm that brewery wastewater sludge can be converted into a sustainable, low-cost adsorbent for phosphate removal. The adsorption process is governed by surface chemistry and electrostatic interactions, with efficiency enhanced under acidic conditions and optimized operational parameters. The sludge-based activated carbon shows monolayer adsorption behavior, follows pseudo-second-order kinetics, and can be reused for multiple cycles. These results are consistent with previous studies on biomass-derived adsorbents and suggest applicability to other breweries generating sludge with similar composition, offering a scalable approach to wastewater treatment and resource valorization.

Conclusion

Activated carbon was synthesized from wastewater treatment sludge obtained from Dashen Brewery via chemical activation using sodium hydroxide and phosphoric acid, followed by pyrolysis. The sludge proved to be an effective precursor for producing activated carbon suitable for phosphate removal from aqueous solutions.

Batch adsorption experiments showed that increasing both contact time and adsorbent dosage significantly enhanced phosphate removal efficiency, whereas higher solution pH reduced adsorption performance. Characterization analyses confirmed that the sludge-based activated carbon possesses a high surface area and abundant surface functional groups, facilitating effective phosphate adsorption.

Process optimization using Design Expert identified optimal conditions of 2.608 g/L adsorbent dose, 120 min contact time, and pH 3, achieving a maximum phosphate removal efficiency of approximately 80%. Adsorption isotherm analysis revealed that the experimental data were best described by the Langmuir model, indicating monolayer adsorption on a homogeneous surface. Kinetic studies further demonstrated that phosphate adsorption follows the pseudo-second-order model, suggesting chemisorption as the dominant mechanism.

Regeneration experiments showed that the adsorbent retained over 50% of its initial removal efficiency after three reuse cycles, indicating satisfactory reusability for practical applications.

In conclusion, chemically modified sewage sludge represents a low-cost, sustainable, and effective adsorbent for phosphate removal from wastewater. This approach not only improves water quality but also provides a practical strategy for valorizing industrial waste, demonstrating the environmental and economic potential of sludge-based activated carbon as a sustainable solution for wastewater treatment.

Acknowledgement

The work was partially supported by the Polish Ministry of Science and Higher Education (grant number 0911/SBAD/2607).

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Wykorzystanie osadu z oczyszczalni ścieków browarniczych do usuwania fosforanów: przygotowanie, optymalizacja i właściwości chemicznie aktywowanego węgla

Streszczenie. Zrzut fosforu z przemysłowych ścieków, w tym z przemysłu browarniczego, w znacznym stopniu przyczynia się do eutrofizacji i pogorszenia jakości ekosystemów wodnych. Dlatego istotne jest opracowanie zrównoważonych i niskokosztowych materiałów do usuwania fosforu. W niniejszym badaniu oceniano węgiel aktywowany otrzymany z osadu ściekowego pochodzącego z oczyszczalni Dashen Brewery (Gondar, Etiopia) pod kątem usuwania fosforu z roztworów wodnych. Osad został chemicznie aktywowany kwasem fosforowym (H_3PO_4) i wodorotlenkiem sodu (NaOH), a następnie poddany karbonizacji termicznej. Charakterystykę fizykochemiczną wykonano metodami analizy powierzchni BET, spektroskopii FT-IR, określenia punktu zerowego ładunku (pHPZC) oraz analizy przybliżonej (proximate analysis). Węgiel aktywowany H_3PO_4 wykazał dobrze rozwiniętą strukturę porowatą o powierzchni 427,05 m^2/g i wyższą efektywność usuwania fosforu w porównaniu z próbkami aktywowanymi NaOH. Optymalizację przeprowadzono metodą powierzchni odpowiedzi (RSM-CCD), wskazując optymalne warunki: pH 3, czas kontaktu 120 min oraz dawkę adsorbentu 2,61 g/L, osiągając 80,3% usuwania fosforu i pojemność adsorpcyjną 13,6 mg/g. Kinetyka adsorpcji odpowiadała modelowi pseudo-drugiego rzędu, co sugeruje chemisorpcję. Badania regeneracji wykazały, że adsorbent zachował ponad 50% początkowej efektywności po trzech cyklach. Wyniki pokazują, że osad browarniczy może być skutecznie przekształcony w efektywny adsorbent do usuwania fosforu, z możliwością zastosowania w innych browarach produkujących osad o podobnym składzie.