

Article

Sustainable Low-Temperature Metakaolin-Based Reactive Materials for Phosphate Removal from Agricultural Drainage Water

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Abstract

Phosphate concentrations in agricultural drainage water frequently exceed those observed in municipal wastewater and, when discharged directly into river systems, pose a significant risk to their ecological status and potential. Developing cost-effective and scalable solutions for phosphate interception at the source is therefore essential for achieving the water quality goals outlined in environmental sustainability frameworks. This study evaluated the phosphate removal capacity of calcium hydroxide-modified metakaolin-based reactive materials as a sustainable approach to limiting agricultural nutrient loads entering river ecosystems. Two synthesis methods were compared: a fusion method and a low-temperature method. The resulting materials—metakaolin (M), low-temperature synthesized metakaolin (MLT), and Ca(OH)₂-modified low-temperature metakaolin (CaMLT)—were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), textural property analysis, and scanning electron microscopy (SEM). Phosphate removal performance was evaluated in batch experiments under varying reactive material dosages (2.5–10.0 g·L^{−1}), initial phosphate concentrations (1.0–7.0 mg·L^{−1}), and contact times (1–144 h). The CaMLT material achieved the highest phosphate removal efficiency of 56% at a phosphate concentration of 1.0 mg·L^{−1}, a dose of 10.0 g·L^{−1}, and a contact time of 144 h. At higher phosphate concentrations (3.0 and 7.0 mg·L^{−1}), removal efficiencies decreased to 23% and 21%, respectively, under the same experimental conditions. The results were benchmarked against data reported in the literature. The findings indicate that low-temperature synthesized metakaolin modified with calcium hydroxide demonstrates potential as a reactive material for phosphate capture in agricultural drainage systems, offering a promising pathway toward more sustainable water resource management and freshwater ecosystem protection.



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1. Introduction

Eutrophication of surface waters constitutes one of the most pressing environmental challenges associated with the progressive degradation of water resource quality and represents a critical barrier to achieving sustainable water management. Excessive nutrient

loading, particularly phosphorus, leads to algal blooms, disrupts the functioning of aquatic ecosystems, contributes to biodiversity loss, and compromises water quality required for economic and municipal purposes. Although eutrophication has conventionally been associated with lentic systems such as lakes, an increasing deterioration in the ecological status of lotic surface waters has also been documented, with phosphorus remaining among the principal drivers of anthropogenic pressure on these systems [1].

Agriculture is widely recognized as one of the most significant sources of phosphorus emission to the aquatic environment, accounting for a substantial proportion of the total phosphorus load delivered to riverine systems [2]. Phosphorus losses originate both from point sources associated with farmstead operations and from non-point (diffuse) sources resulting from the fertilization of agricultural land [3]. Subsurface drainage systems and drainage ditches are of particular significance in this context, as they establish a direct hydrological connection between the soil profile and surface water receivers, thereby facilitating the rapid transport of dissolved phosphorus fractions to downstream water bodies [4,5]. In numerous instances, the acceleration of hydrological outflow from agricultural catchments may exert an influence on surface water quality comparable to that of fertilization intensity itself [5]. Mitigation of phosphorus losses from agricultural systems is therefore a prerequisite not only for fulfilling the requirements of the Water Framework Directive but also for advancing the Sustainable Development Goals concerned with water resource protection (SDG 6), responsible production and consumption (SDG 12), and the conservation of terrestrial and aquatic ecosystems (SDG 15) [6,7].

Among the most promising strategies for limiting phosphorus runoff, consistent with the principles of sustainable and resource-efficient water management, is the deployment of reactive materials directly within drainage infrastructure or within landscape-scale structures designed for the treatment of agricultural runoff [6,7]. Such materials enable phosphate capture via adsorption, ion exchange, or precipitation of phosphorus-bearing compounds, thereby attenuating phosphorus transport to receiving waters [2,8]. Natural materials, industrial products, and waste-derived materials have all been implemented for this purpose, reflecting a broader shift toward circular-economy approaches in environmental engineering. The most frequently employed natural materials include calcareous-siliceous “opoka” rock, limestone, apatite, and natural zeolites [9–13]. Among industrial materials, lightweight expanded aggregates and crushed concrete have found extensive application [11], whereas fly ash, steel slag, and other industrial by-products represent important waste-derived alternatives [11,14–16].

The phosphorus-removal efficacy of reactive materials is attributable primarily to the presence of calcium, aluminum, or iron, which mediate the principal phosphate-binding mechanisms [2,3]. Aluminosilicate materials, including zeolites, have attracted considerable scientific interest owing to their well-developed porous architecture, high specific surface area, and pronounced ion-exchange capacity, properties that underpin their widespread application in water treatment technologies [4–7]. Reported phosphate removal efficiencies for appropriately modified zeolites exceed 80%, with values approaching 100% documented under certain experimental conditions [4,6]. However, the predominantly negative surface charge of zeolites limits their affinity toward phosphate anions [8]. Consequently, a range of chemical modification strategies has been developed with the objective of enhancing the phosphorus affinity of these materials while preserving their favorable environmental and economic profile.

One of the most extensively investigated modification strategies involves the enrichment of aluminosilicate matrices with calcium compounds. Calcium-bearing materials, including limestone, concrete-derived products, and calcium-enriched sorbents, exhibit pronounced phosphorus-removal capacity, attributable to surface adsorption mechanisms

in conjunction with the precipitation of sparingly soluble calcium phosphate phases [11,17]. Relative to modifications employing lanthanum, zirconium, aluminum, or iron compounds, calcium-based modifications offer notable advantages in terms of cost-effectiveness, procedural simplicity, and environmental compatibility—criteria of particular relevance when assessing the sustainability of candidate materials for large-scale field application [2,18]. Calcium hydroxide, owing to its widespread availability and long-established application in water treatment technology, represents a particularly attractive and low-cost modifying agent for sorptive materials [18].

Considerable research attention has recently been directed toward materials derived from metakaolin, a mineral resource that can be obtained through the processing of widely available kaolinitic clays. Metakaolin, a highly reactive aluminosilicate phase generated through the thermal activation of kaolinite, is characterized by an elevated content of reactive silicon and aluminum species [19]. These properties render it a valuable precursor in the synthesis of zeolitic materials applied as adsorbents and ion exchangers. Zeolitic phases including zeolite A, zeolite X, zeolite P, and sodalite have been successfully synthesized from metakaolin precursors, exhibiting favorable sorption characteristics and substantial application potential within environmental engineering [20,21].

A persistent challenge associated with the production of zeolitic materials, and one of direct relevance to their sustainability assessment, concerns the energy intensity inherent to conventional synthesis pathways. Conventional synthesis routes typically incorporate a fusion processes or hydrothermal processing under elevated temperature regimes, entailing substantial energy expenditure and a correspondingly elevated carbon and environmental footprint. Accordingly, the development of low-temperature, low-energy synthesis routes is regarded as a priority research direction within the broader framework of sustainable sorptive material [22]. Synthesis conducted under milder thermal conditions has the potential to reduce energy-related costs and associated greenhouse gas emissions while enhancing the economic and technical feasibility of large-scale implementation of reactive materials within water-quality protection systems.

Furthermore, the physicochemical properties of metakaolin-derived materials can be effectively tailored through the incorporation of calcium compounds. Prior investigations have addressed, *inter alia*, the modification of clinoptilolite with calcium chloride [12,23], the modification of bentonite and zeolites with calcium hydroxide [24], $\text{Ca}(\text{OH})_2$ -based ceramic materials [25] and calcium-enriched biochars [26]. In the majority of these studies, calcium incorporation enhanced phosphate-binding capacity through the formation of thermodynamically stable calcium–phosphate phases [27].

Despite the growing body of literature concerning phosphorus sorbents, comparatively limited attention has hitherto been devoted to materials synthesized from metakaolin via low-temperature methods and subsequently modified with calcium hydroxide for application in the treatment of agricultural drainage waters. Knowledge regarding the removal efficacy of such materials at phosphate concentrations representative of drainage outflows—typically substantially lower than those characteristic of municipal wastewater—remains particularly scarce, despite the practical importance of such conditions for the sustainable management of agricultural water quality [28].

The objective of the present study was to synthesize and characterize reactive materials derived from metakaolin via a low-temperature, energy-efficient method and subsequently modified with calcium hydroxide. The influence of synthesis and modification parameters on the physicochemical properties of the resulting materials, as well as on their phosphate-removal capacity within the concentration range characteristic of agricultural drainage waters, was systematically evaluated. The obtained findings were employed to assess the potential of the developed materials as sustainable, low-cost sorbents for

mitigating phosphorus losses from agricultural land and for protecting aquatic ecosystems against eutrophication, in line with the broader objectives of sustainable agricultural water management and circular resource use.

2. Materials and Methods

To systematize the overall research process, a detailed research workflow was developed for the purposes of this study (Figure 1). The proposed roadmap reflects the iterative character of the constituent phases, encompassing the formulation of the research problem, the selection of appropriate methodological approaches, and the subsequent verification, interpretation, and evaluation of the potential of the obtained results for sustainable practical implementation.

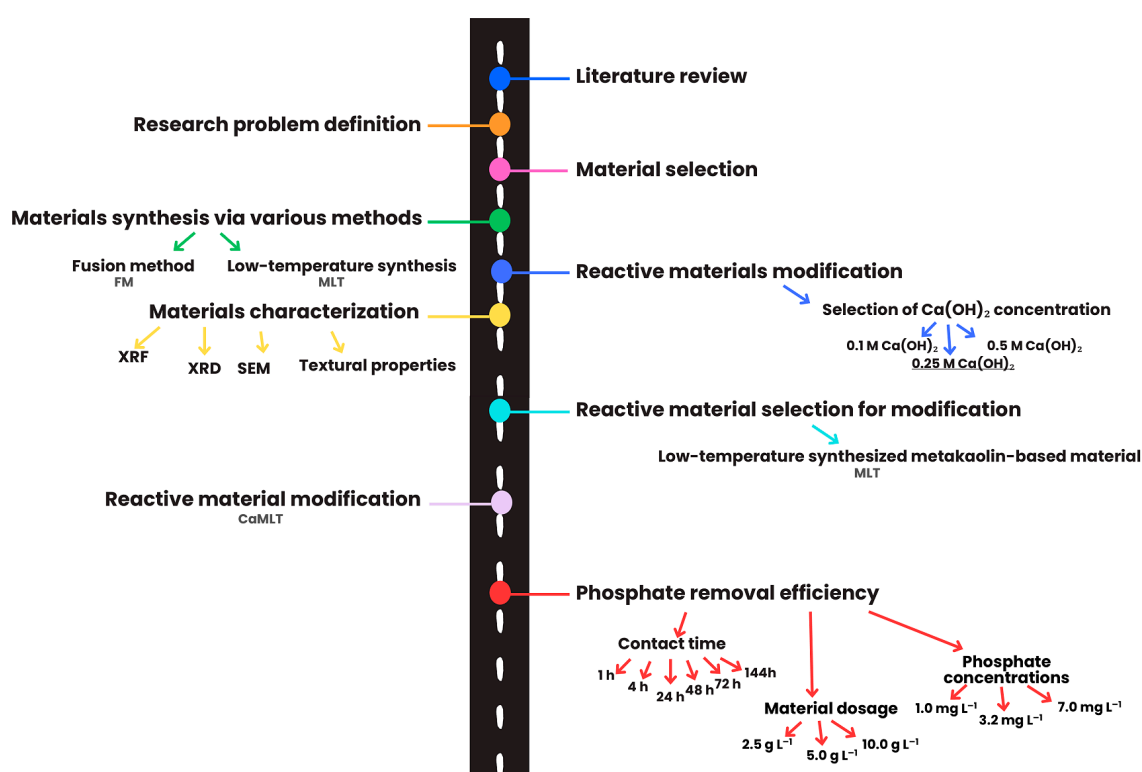


Figure 1. Research roadmap illustrating the main phases and sequential steps of the study.

2.1. Raw Materials

Metakaolin is a mineral obtained by calcining natural kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$ at temperatures ranging from 550 °C to 950 °C. Kaolinite is a clay mineral with double-layer packet structure [28,29]. The calcination process causes a loss of structural water and leads to structural reorganization. However, it should be noted that the calcination conditions significantly influence the formation of metakaolin. The optimal conditions for metakaolin formation were discussed by other authors, who concluded that calcination should be carried out at temperatures between 600 and 800 °C [19–21]. Calcination at higher temperatures causes the formation of mullite and cristobalite, which are inert components. A properly conducted calcination process yields metakaolin, which constitutes a suitable source of silica and aluminum for subsequent zeolite synthesis [22,23].

The metakaolin used in this study was supplied by Rominco Polska LLC (Kraków, Poland), produced by calcinating pure Chinese kaolinite. The chemical composition of the metakaolin determined by X-ray fluorescence spectroscopy (XRF) is presented in Table 1. Metakaolin had the highest content of SiO_2 and Al_2O_3 among all identified oxides; together,

these two oxides accounted for 91.34% of the material, confirming that metakaolin was a proper choice as a source of Si-Al for zeolite synthesis [30].

Table 1. Chemical composition of metakaolin (M) determined by XRF (wt.%).

Compound %	M
P ₂ O ₅	0.09
SiO ₂	48.10
TiO ₂	0.46
Al ₂ O ₃	43.24
Fe ₂ O ₃	1.11
SO ₃	0.02
CaO	0.13
MgO	0.30
MnO	0.02
Na ₂ O	0.52
K ₂ O	1.51
Rb ₂ O	0.01
ZrO ₂	0.03
Cr ₂ O	0.01
Ga ₂ O ₃	0.01
ZnO	0
SrO	0.02
BaO	0.04
Ig	4.37
pH	6.57
Sum	99.99

Sodium hydroxide (NaOH) flakes, with a purity above 98%, were purchased from ChemiKam (Będzin, Poland).

2.2. Synthesis of Metakaolin-Derived Reactive Materials

The zeolites used in this study were obtained using two methods: the fusion method and the low-temperature method. Detailed sample designations, including the synthesis methods used and the type of modification applied to each reactive material, are given in Table 2.

Table 2. Sample designations according to the synthesis method and the modification applied to the reactive materials.

Sample	Synthesis Method	Modification
M	-	-
MF	Fusion	-
MLT	Low-temperature	-
CaMLT	Low-temperature	Ca(OH) ₂ solution

2.2.1. Low-Temperature Synthesis

To produce zeolites by the low-temperature method, a 3 M sodium hydroxide aqueous solution was first prepared from sodium hydroxide (NaOH) flakes. The NaOH-solution-to-precursor ratio was set at 0.1 L per 10 g of metakaolin. The mixtures were tightly sealed in 1 L polypropylene cylindrical containers and left at an ambient temperature (21 °C) for 30 days. The containers were mixed intensively for 15 min every day at 150 rpm. After

zeolitization, the samples were filtered to remove residual activation solution, washed with approximately 10 L of distilled water to reach a pH of about 10, and dried at 105 °C for 6 h.

2.2.2. Fusion Synthesis

The fusion synthesis of zeolites consisted of several phases. First, metakaolin and an alkaline activator (technical sodium hydroxide, purity above 98%) were combined at a ratio of 0.83 in a 0.1 L fireproof melting pot. The mixture was then placed in a muffle furnace (model SX2–2.5–12, Shanghai Lichen Bangxi Instrument Technology Co., Ltd., Shanghai, China) under air conditions at 170 °C for 4 h. After sintering, the resulting material was ground and transferred to a 1 L cylindrical glass vessel. Water was added at 4.5 mL per 1.0 g of sintered material, and the mixture was stirred for 1 h using an ultrasonic stirrer. The vessel was then placed in a laboratory drying apparatus (Chemland, Stargard, Poland) firstly for 24 h at 100 °C for the activation, and then for a further 24 h at 60 °C for crystallization. After zeolitisation, the samples were cooled to room temperature, filtered using approximately 10 L of distilled water to bring the pH to 10, and dried at 105 °C for 6 h.

A comparison of both applied synthesis methods is shown in Figure 2. The main differences between the fusion and low-temperature methods relate to synthesis duration and energy consumption: the low-temperature method requires a longer synthesis time but consumes less energy than the fusion method.

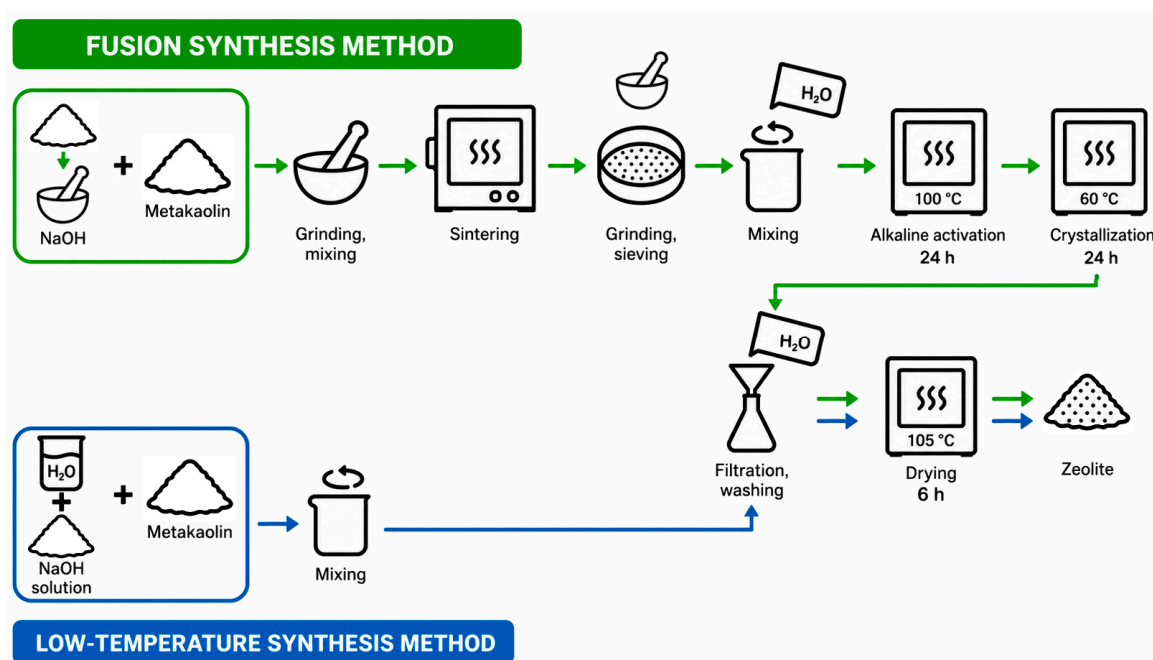


Figure 2. Schematic diagram of zeolite synthesis methods.

2.2.3. Modification with Calcium Hydroxide

To determine the optimal molar concentration of $\text{Ca}(\text{OH})_2$ solution for the modification of reactive materials, the following experiment was designed.

A zeolite based on metakaolin, synthesised by a low-temperature method, was selected as a reactive material for modification with $\text{Ca}(\text{OH})_2$ solution. The molar concentrations of the $\text{Ca}(\text{OH})_2$ solutions were selected on the basis of the experimental work of Mitrogiannis et al. [6] and were set at 0.1 M, 0.25 M, and 0.5 M.

The applied zeolite to $\text{Ca}(\text{OH})_2$ solution ratio was 1:10, and the process was carried out at a temperature of 20 °C. An appropriate amount of $\text{Ca}(\text{OH})_2$ was first added to distilled water, and the mixture was stirred with a magnetic stirrer for 1 h to prepare $\text{Ca}(\text{OH})_2$ solutions of specified molar concentrations. Defined quantities of reactive material were

placed in vials, and the $\text{Ca}(\text{OH})_2$ solution was then added. The vials were shaken at 150 rpm for 24 h, and the resulting suspension was centrifuged at 4500 rpm for 10 min. The supernatant was decanted, and distilled water was added to the samples remaining in the vessels. The samples were then shaken at 150 rpm for 10 min. Next, the samples were transferred from each flask into a plastic-corked bottle, then filled with 1 L of water, and shaken again at 150 rpm for 1 h. The bottles were left to stand for 15 min, and the suspension was then filtered using a water vacuum pump and fine filter paper. The resulting samples were dried at 105 °C and washed repeatedly until the pH of the rinse water was similar to the pH of the zeolite before modification.

In the next step, a preliminary experiment was carried out to assess the phosphate removal efficiency of reactive materials modified with $\text{Ca}(\text{OH})_2$ solutions at molar concentrations of 0.1 M, 0.25 M, and 0.5 M. The tests were conducted using parameters established on the basis of previous studies: a dose of $5.0 \text{ g}\cdot\text{L}^{-1}$, phosphate concentrations of approximately 1.0 and $7.0 \text{ mg}\cdot\text{L}^{-1}$, and an initial solution pH of 7 [18,24–26]. Phosphate concentrations in the samples were measured after 24, 48, 72 and 144 h of contact times between the modified materials and the phosphate solutions [6].

The reactive materials modified with the three molar concentrations of $\text{Ca}(\text{OH})_2$ solution in this preliminary experiment are listed in Table 3. Phosphate removal efficiency was evaluated in order to determine the optimal modifier concentration for reactive materials.

Table 3. Designations of samples used in the preliminary $\text{Ca}(\text{OH})_2$ modification experiment.

Sample Designation	Molar Concentration of $\text{Ca}(\text{OH})_2$ Solutions	Synthesis Method	Modifier
0.1 M CaMLT	0.10	Low-temperature	$\text{Ca}(\text{OH})_2$ solutions
0.25 M CaMLT	0.25		
0.5 M CaMLT	0.50		

The modified reactive materials ($1000 \pm 2 \text{ mg}$) were placed in 0.25 L black plastic bottles, and 0.2 L of phosphate solution was added. The components were mixed for 60 s, and the bottles were then sealed with a cork to minimize evaporation. Phosphate concentrations were measured after 24, 48, 72, and 144 h of contact time.

2.3. Materials Characterization

The mineralogical composition of the metakaolin and zeolite samples was determined by X-ray diffraction (XRD) using a Rigaku SmartLab diffractometer (Rigaku Corporation, Tokyo, Japan). Phase composition was identified using the powder (Debye-Scherrer) method. Diffractograms of all samples were recorded using a reflection graphite monochromator with $\text{Cu-K}\alpha$ radiation, over a scan range of $5\text{--}70^\circ$ (2θ), with a counting time of 1 s per step. Quantitative analysis was performed on the basis of the calculated interplanar distances using XRAYAN v4.1.3 software with the ICDD (International Centre for Diffraction Data) database.

The chemical composition of the samples was determined by X-ray fluorescence (XRF) spectrometry (PANalytical, Almelo, The Netherlands). Spectral quality was assessed by identifying spectral lines and possible line overlaps, on the basis of which the analytical lines were selected. Semi-quantitative analysis was performed over the fluorine–uranium (F–U) range using SQX v5 software (fundamental parameters approach). Samples were prepared as pressed pellets with a binder, using a sample-to-binder ratio of 4.5:1.5.

The textural properties of the raw material, the zeolite, and the modified zeolite were determined from nitrogen adsorption–desorption isotherms recorded on an ASAP 2020 analyzer (Micromeritics, Norcross, GA, USA). Samples were degassed at 150 °C for 12 h before

isotherm measurement to remove vapours and gases accumulated on the sample surface. Specific surface area was determined by the Brunauer–Emmett–Teller (BET) method. Total pore volume was determined at a relative pressure of 0.99. Microporosity and mesoporosity were determined using the Dubinin–Radushkevich (DR) and Barrett–Joyner–Halenda (BJH) methods, respectively. Macroporosity was evaluated by comparing the difference between the total pore volume and the sum of the micropore and mesopore volumes.

Scanning electron microscopy (SEM) was used to examine sample morphology. Prior to observation, samples were dried to constant weight, placed on the carbon support, and coated with a gold layer using JEOL JEE-4X vacuum evaporator (JEOL, Tokyo, Japan).

2.4. Batch Phosphate Removal Experiments

Phosphate removal experiments were carried out to assess and compare the phosphate removal performance of the modified reactive material, CaMLT—a low-temperature synthesized, metakaolin-based material modified with 0.25 M Ca(OH)₂.

Modification and phosphate removal tests were carried out using a static method in a closed system, in which fixed volumes of phosphate solution were reacted with the zeolite material. The reactions lasted 1, 4, 24, 48, 72, and 144 h, depending on the variant [6].

Based on the analysis of the phosphate concentrations typical of drainage water, three initial phosphate concentrations were used: approximately 1.0, 3.2 and 7.0 mg·L^{−1}. The phosphate solutions (KH₂PO₄) were prepared by dissolving an appropriate amount of potassium dihydrogen phosphate in distilled water. The effect of the initial solution pH on phosphate removal efficiency was evaluated before the main adsorption experiments were started. The tests were carried out at pH 6, 7, and 8, corresponding to the range of pH values typically observed in agricultural drainage waters. Since the obtained results showed only minor differences between the analyzed pH variants, further experiments were conducted at pH = 7 as a representative value.

The contents of the bottles were mixed for 60 s and then corked to prevent evaporation. Phosphate concentration in each bottle was measured after 1, 4, 24, 48, 72, 144 h of contact time. The collected samples were filtered through a 0.45 µm syringe filter.

Based on a review of the literature, three doses of modified reactive material were selected: 2.5, 5.0 and 10.0 g·L^{−1}. Air-dried samples of the modified reactive materials, at dose levels of 500, 1000, and 2000 ± 2.0 mg, were placed in 0.25 L plastic bottles and immersed in 0.20 L of phosphate solution at the desired concentration. The stated accuracy (± 2.0 mg) corresponds to the precision of the analytical balance used (RADWAG, Radom, Poland). The applied doses correspond to solid-to-solution ratios of 2.5, 5.0, and 10.0 g·L^{−1}.

2.5. Analytical Methods and Data Analysis

To determine kinetic parameters and understand the mass transfer mechanism in the adsorption process, the experimental data were subjected to mathematical analysis using three theoretical models: the pseudo-first-order (PFO) model, the pseudo-second-order (PSO) model, and the Weber–Morris intraparticle diffusion model. Model parameters were determined by non-linear regression, which avoids the mathematical errors and distortions of the experimental error structure that frequently arise from the traditional linearization of equations. The non-linear forms of the pseudo-first-order and pseudo-second-order models are described by Equations (1) and (2), respectively:

$$q_t = q_e (1 - e^{-k_1 t}) \quad (1)$$

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

where

q_t and q_e ($\text{mg}\cdot\text{g}^{-1}$) are the amounts of adsorbate retained per unit mass of adsorbent at time t and at equilibrium, respectively,

t (h) is the phase contact time,

k_1 (h^{-1}) is the rate constant of the pseudo-first-order model,

k_2 ($\text{g}\cdot\text{mg}\cdot\text{h}^{-1}$) is the rate constant of the pseudo-second-order model.

The rate-limiting steps and the contribution of pore diffusion were examined using the Weber–Morris intraparticle diffusion model, described by Equation (3):

$$q_t = k_{id} \cdot t^{0.5} + C \quad (3)$$

where

k_{id} ($\text{mg}\cdot(\text{g}\cdot\text{h}^{0.5})^{-1}$) is the intraparticle diffusion rate constant,

C ($\text{mg}\cdot\text{g}^{-1}$) is a constant related to the thickness of the boundary layer (liquid film diffusion resistance).

The structural parameters of the models— q_e , k_1 , k_2 , k_{id} and C —were optimized by minimizing the sum of squared errors (SSE) between experimental and theoretically calculated values. The coefficient of determination R^2 was used as the criterion for assessing the quality of fit of the regression curves to the measured data. All computational and graphical procedures were carried out using Microsoft Excel.

The adsorption equilibrium was analyzed using two classical isotherm models: the Langmuir model and the Freundlich model. Model parameters were determined by non-linear regression.

The non-linear form of the Langmuir model, which assumes monolayer adsorption on an energetically homogeneous surface with no interactions between adsorbed molecules, is described by Equation (4):

$$q_e = \left(\frac{q_{\max} K_L C_e}{1 + K_L C_e} \right) \quad (4)$$

where

q_e is the equilibrium adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$),

C_e is the equilibrium concentration of the adsorbate in solution ($\text{mg}\cdot\text{L}^{-1}$),

$q_{\max}$ is the maximum monolayer adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$)

K_L is the Langmuir constant related to the affinity of the adsorbent for the adsorbate ($\text{L}\cdot\text{mg}^{-1}$).

The non-linear form of the Freundlich model, which describes multilayer adsorption on an energetically heterogeneous surface, is given by Equation (5):

$$q_e = K_F \cdot C_e^{1/n} \quad (5)$$

where

K_F is the Freundlich constant representing adsorption capacity ($\text{mg}\cdot\text{g}^{-1})(\text{L}\cdot\text{mg}^{-1})^{1/n}$,

n is a dimensionless heterogeneity parameter whose value reflects the strength of the adsorption process.

Phosphate removal efficiency was calculated using Equation (6):

$$\text{Removal efficiency}(\%) = \left(\frac{C_i - C_f}{C_i} \right) \cdot 100\% \quad (6)$$

where C_i is the initial phosphate concentration ($\text{mg}\cdot\text{L}^{-1}$), C_f is the final phosphate concentration ($\text{mg}\cdot\text{L}^{-1}$) [31].

Adsorption capacity (q , $\text{mg}\cdot\text{g}^{-1}$) was calculated according to Equation (7):

$$q = \frac{(C_i - C_f) \cdot V}{m} \quad (7)$$

where C_i and C_f are the initial and final phosphate concentrations ($\text{mg}\cdot\text{L}^{-1}$), respectively, V is the volume of the solution (L) and m is the mass of adsorbent used (g).

Initial and final phosphate concentrations in solution were determined by calorimetric analysis using ammonium molybdate and ascorbic acid [32,33]. Absorbance was measured at a wavelength of 870 nm using a Hitachi U-1800 spectrophotometer (Hitachi, Tokyo, Japan). All measurements were performed in triplicate, with samples taken from three separate bottles.

The pH of the phosphate solutions was measured using a CX-551 multifunction microcomputer instrument (Elmetron, Zabrze, Poland).

3. Results

3.1. Chemical and Mineralogical Characterization

The chemical composition of the zeolites synthesized by the low-temperature method, as well as of the reactive material after modification, is shown in Table 4. Comparing the results for MLT and 0.25 M CaMLT, it can be seen that the applied modification increased the CaO content from 1.79% to 14.57%. This change was also reflected in the SEM images of MLT and 0.25 M CaMLT, which showed different sample morphologies. The pH of the metakaolin was 6.57 (Table 1); the use of sodium hydroxide during zeolite synthesis increases the pH to 9.82. In contrast, the pH of reactive materials before and after modification was comparable.

Table 4. Chemical composition of MLT and 0.25 M CaMLT.

Compound %	Material	
	MLT	0.25 M CaMLT
P ₂ O ₅	0.02	0.02
SiO ₂	35.22	30.39
TiO ₂	0.19	0.12
Al ₂ O ₃	31.42	26.72
Fe ₂ O ₃	0.96	0.88
SO ₃	0.01	0.36
CaO	1.79	14.57
MgO	0.44	0.53
MnO	0.01	0.02
Na ₂ O	10.08	2.62
K ₂ O	1.04	0.83
Rb ₂ O	0.01	0.01
ZrO ₂	0.03	0.03
Cr ₂ O	0.01	0
Ga ₂ O ₃	0	0
ZnO	0.01	0.01
SrO	0.02	0.02
BaO	0.04	0
Ig	18.49	22.63
pH	9.82	9.95
Sum	99.97	99.97

The results of the XRD analysis are presented in Figure 3. An amorphous hump can be observed in all materials investigated. However, in the metakaolin this hump was centered at approximately 2θ 20°, whereas in both types of zeolite material it was shifted to higher angular positions. These observations are consistent with results reported by other authors [34,35], indicating that a polycondensation reaction of silicate and aluminate occurred, leading to the formation of a new amorphous phase. Based on the results, metakaolin can be considered to consist mainly of muscovite ($\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH},\text{F})_2$, ref. code: 00-006-0263) and kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, ref. code: 01-078-2110), together with smaller amounts of quartz (SiO_2 , ref. code: 01-075-8320) and andalusite (Al_2SiO_5 , ref. code: 00-018-0036).

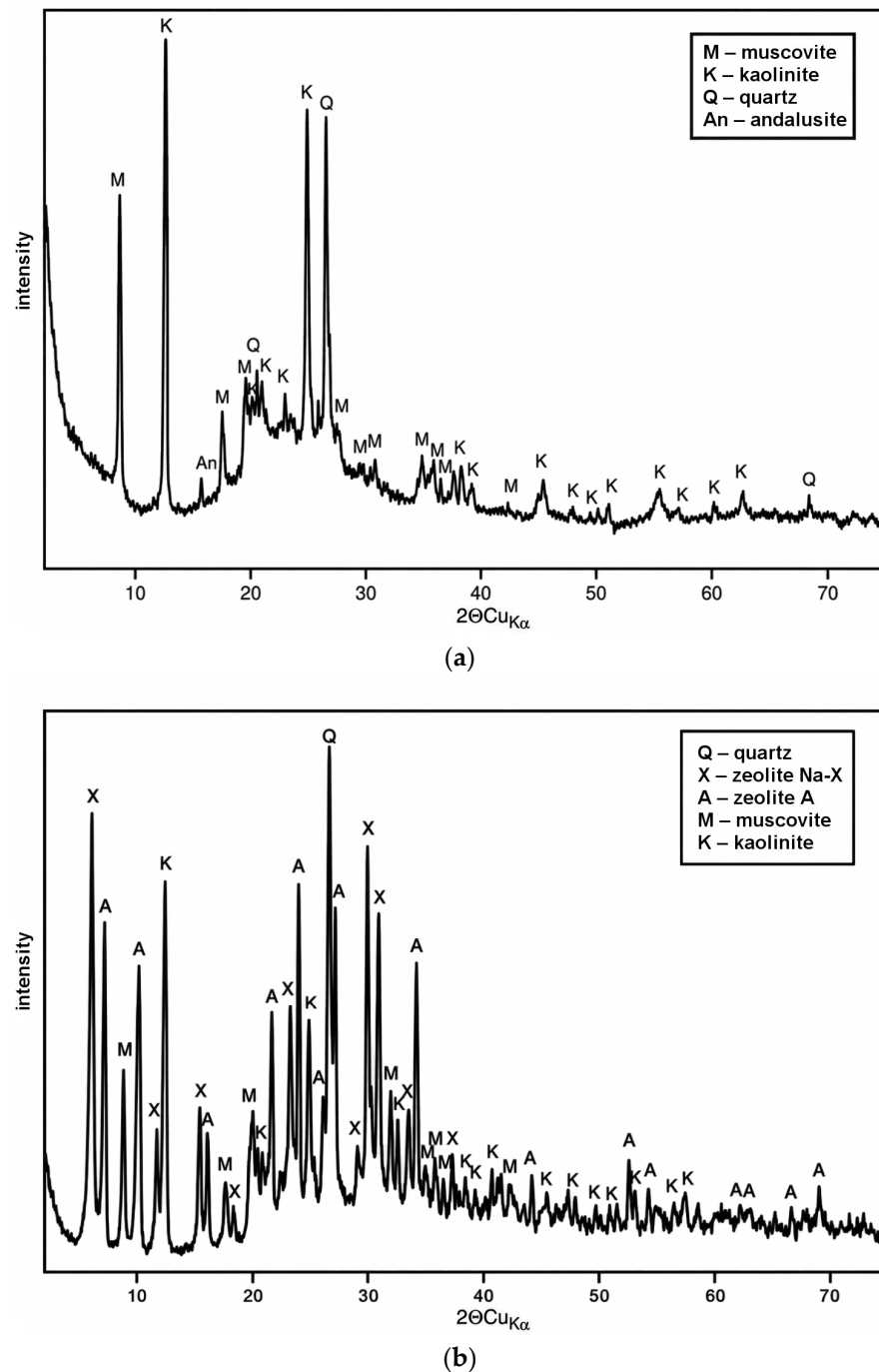


Figure 3. Cont.

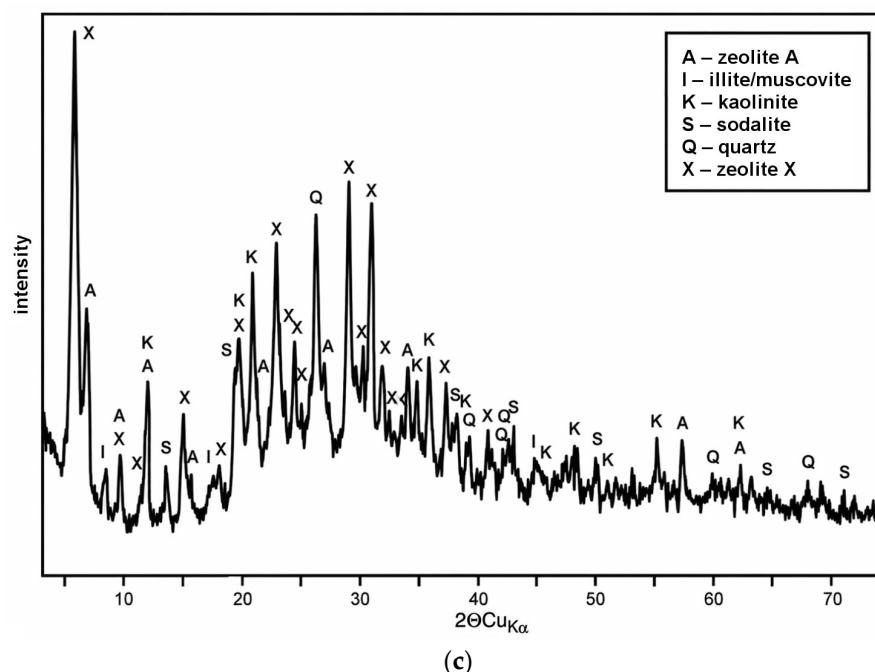


Figure 3. X-ray diffraction (XRD) patterns of (a) M, (b) MLT, and (c) 0.25 M CaMLT.

The material obtained by low-temperature synthesis consisted mainly of zeolite A and zeolite Na-X. Quartz was also identified, representing unreacted residue from the raw material. Similar synthesis products were reported by other authors [36–40]. In the modified zeolites (0.25 M CaMLT), zeolite A and zeolite X were present in the highest amounts, together with kaolinite, illite, and sodalite.

3.2. Morphology (SEM) and Textural Properties

Figure 4 shows SEM images of metakaolin (a,b), MF (c,d), MLT (e,f), and 0.25 M CaMLT (g,h). Metakaolin grains have a plate-like shape and occur individually or as agglomerates. The metakaolin plates do not exceed 10 μm in size, and their edges are sharp or partially rounded; spherical grains are not present in the raw material. Zeolite synthesis by the low-temperature method (Figure 4e,f) produced crystals forming irregularly shaped agglomerates that generally resemble plates [41,42]. The morphology of the material synthesized by the fusion method (Figure 4c,d) is characterized by fewer visible crystals and a predominantly amorphous phase, compared with the material obtained by the low-temperature method (Figure 4e,f). In the modified reactive material (Figure 4g,h), the 0.25 M $\text{Ca}(\text{OH})_2$ solution reacted with the MLT matrix producing a dense layer on the crystal surface. The crystals of the synthesized and $\text{Ca}(\text{OH})_2$ -modified material can act as carriers and owing to their microporous structure, may also contribute directly to phosphate removal [43].

The textural properties of metakaolin and of the zeolite materials obtained by the fusion method, the low-temperature method and the low-temperature method after modification are presented in Table 5. The specific surface area increased after zeolitization compared with the precursor material. The greatest increase in specific surface area, 24-fold, was achieved using the low-temperature synthesis method; micropores were the dominant pore type in the MLT sample. Synthesis by the fusion method resulted in a smaller increase in specific surface area, of approximately 26% compared with metakaolin. The reactive material selected for modification with $\text{Ca}(\text{OH})_2$ solution was chosen on the basis of these textural results, since specific surface area corresponds to the effective surface area per unit mass and may therefore indicate the availability of potential surface adsorption sites [44].

A comparison of the MLT and 0.25 M CaMLT results shows that the applied modification increases pore volume. Mesopores were the dominant pore type in the 0.25 M CaMLT sample, accounting for 45% of the total pore volume; the micropore content also changed after modification, reaching 28% of the total pore volume.

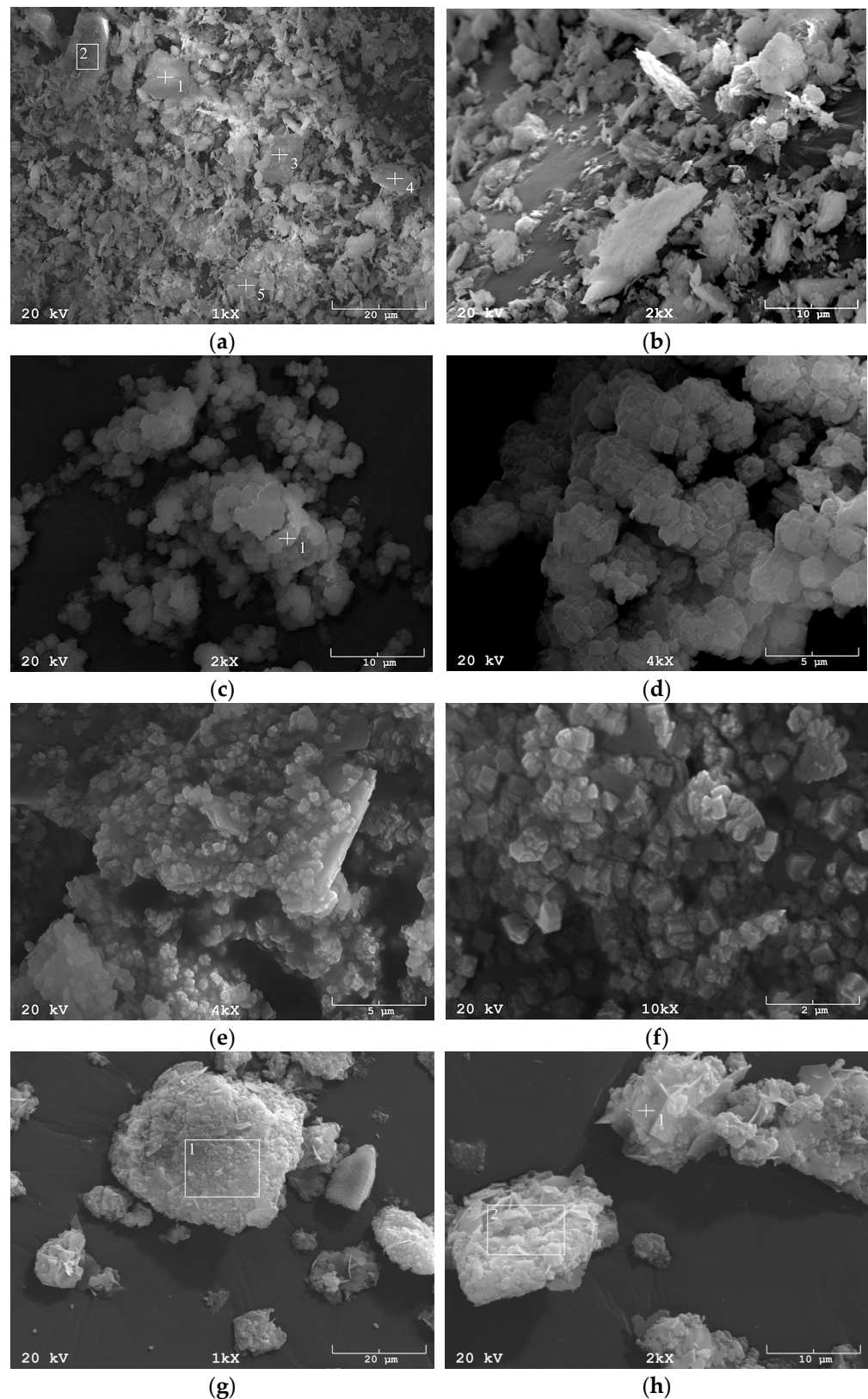


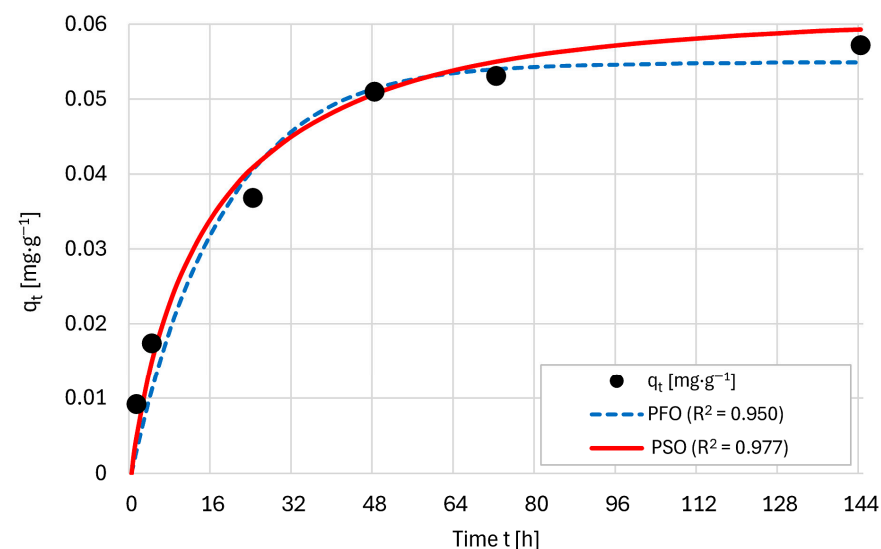
Figure 4. SEM images of (a,b) M, (c,d) MF, (e,f) MLT, and (g,h) 0.25 M CaMLT.

Table 5. Textural parameters of the investigated samples.

Sample	Specific Surface Area $\text{cm}^3 \cdot \text{g}^{-1}$	Total Pore Volume $\text{cm}^3 \cdot \text{g}^{-1}$	Micropore Volume $\text{cm}^3 \cdot \text{g}^{-1}$	Mesopore Volume $\text{cm}^3 \cdot \text{g}^{-1}$
M	13.6	0.069	0.006	0.035
MF	17.2	0.049	0.006	0.036
MLT	328.2	0.187	0.123	0.049
0.25 M CaMLT	267.0	0.358	0.102	0.161

3.3. Adsorption Kinetics

To assess the rate of solute binding and to identify the rate-limiting step of the adsorption process, kinetic experiments were conducted at a fixed adsorbent dose of 0.25 M CaMLT at $10.0 \text{ g} \cdot \text{L}^{-1}$ and an initial adsorbate concentration of $1.021 \text{ mg} \cdot \text{L}^{-1}$. The dependence of the experimental adsorption capacity (q_t , $\text{mg} \cdot \text{g}^{-1}$) on contact time (t , h) is presented in Figure 5.

**Figure 5.** Adsorption kinetics fitted to the pseudo-first-order (PFO) and pseudo-second-order (PSO) models at an adsorbent dose of $10.0 \text{ g} \cdot \text{L}^{-1}$.

The adsorption process proceeded relatively rapidly during the first 24 h, after which it slowed down, reaching a state close to equilibrium after 144 h with a maximum experimental adsorption capacity ($q_{e,\text{exp}}$) of $0.057 \text{ mg} \cdot \text{g}^{-1}$. To analyze the theoretical kinetics of the process in detail, the experimental data were fitted by non-linear regression to three widely used mathematical models: the pseudo-first-order (PFO) model, the pseudo-second-order (PSO) model, and the Weber–Morris intraparticle diffusion model. The kinetic parameters determined, including the rate constants (k_1 , k_2 , k_{id}), the calculated equilibrium adsorption capacities ($q_{e,\text{cal}}$), and the coefficients of determination (R^2), are summarized in Table 6.

A comparison of the coefficients of determination clearly indicates that the PSO model provides a significantly better fit to the experimental data ($R^2 = 0.977$) than the PFO model ($R^2 = 0.950$). Moreover, the equilibrium adsorption capacity calculated from the PSO model ($q_{e,\text{cal}} = 0.061 \text{ mg} \cdot \text{g}^{-1}$) is in good agreement with the experimentally determined value ($q_{e,\text{exp}} = 0.057 \text{ mg} \cdot \text{g}^{-1}$). The better fit of the PSO model ($R^2 = 0.977$) indicates that it most accurately describes the kinetics of the process under the analyzed conditions. This result suggests that the adsorption rate may be controlled by interactions occurring at the material surface; however, a good fit to the PSO model alone does not constitute definitive

evidence of chemisorption. Confirmation of the mechanism would require the application of spectroscopic techniques or surface analysis of the material after adsorption.

Table 6. Kinetic parameters of the adsorption process (dose = 10.0 g·L^{−1}).

Kinetic Model	Parameter	Value	Unit
Experimental data	$q_{e,exp}$	0.057	mg·g ^{−1}
Pseudo-first-order (PFO)	$q_{e,cal}$	0.054	mg·g ^{−1}
	k_1	0.056	h ^{−1}
	R^2	0.950	—
Pseudo-second-order (PSO)	$q_{e,cal}$	0.061	mg·g ^{−1}
	k_1	1.419	g·(mg·h) ^{−1}
	R^2	0.977	—
Weber–Morris intraparticle diffusion	k_{id}	0.005	mg·(g·h ^{0.5}) ^{−1}
	C	0.007	mg·g ^{−1}
	R^2	0.936	—

To examine the mass transfer steps in greater detail and to determine the role of intraparticle diffusion, the data were analyzed using the Weber–Morris intraparticle diffusion model (Figure 6).

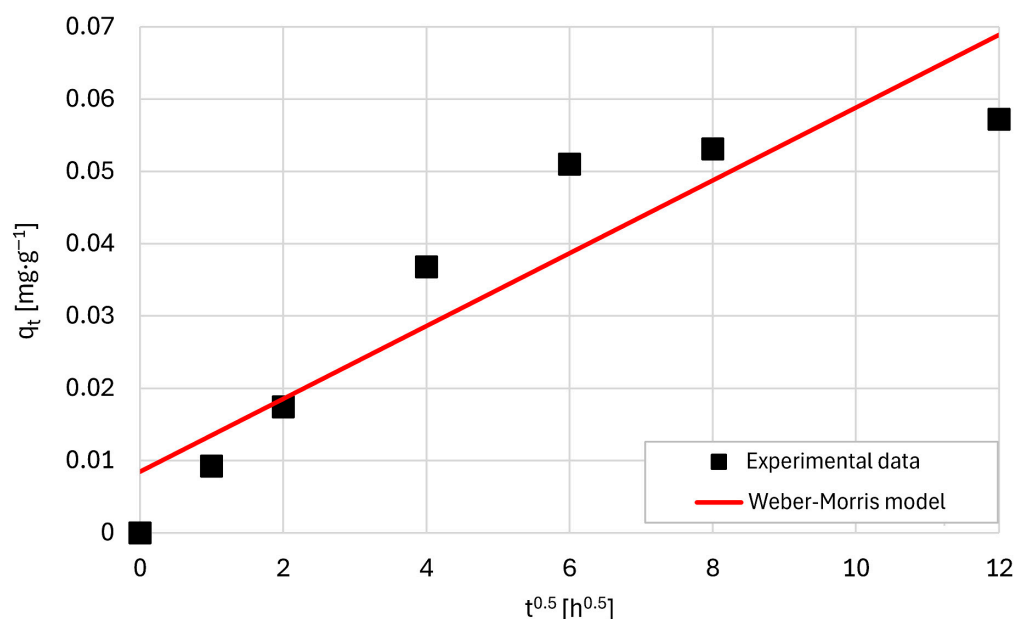


Figure 6. Weber–Morris intraparticle diffusion model fit as a function of the square root of contact time.

According to the assumptions of this model, if intraparticle diffusion were the sole rate-limiting step, the plot of q_t versus $t^{0.5}$ would take the form of a straight line passing through the origin. However, as shown by the data in Table 6, the regression line obtained has a non-zero intercept ($C = 0.007$ mg·g^{−1}). The value of C is directly related to the thickness of the boundary layer—the larger the value of C , the stronger the resistance of that layer.

The results indicate that intraparticle diffusion contributes to the adsorption process but does not constitute the sole rate-limiting step. It can be assumed that mass transport proceeds in multiple stages, involving both diffusion through the boundary layer and transport within the pores of the material.

3.4. Adsorption Equilibrium Isotherms

To characterize the phase equilibrium, describe the structure of the active surface, and determine the maximum sorption capacity of the system, the experimental data were fitted by non-linear regression to the Langmuir and Freundlich models. All isotherm experiments were conducted at a fixed adsorbent dose of $10.0 \text{ g}\cdot\text{L}^{-1}$, ensuring full methodological consistency with the preceding kinetic experiments. The non-linear fits of both models to the experimental data are shown in Figure 7, and the determined isotherm parameters and corresponding R^2 values are summarized in Table 7.

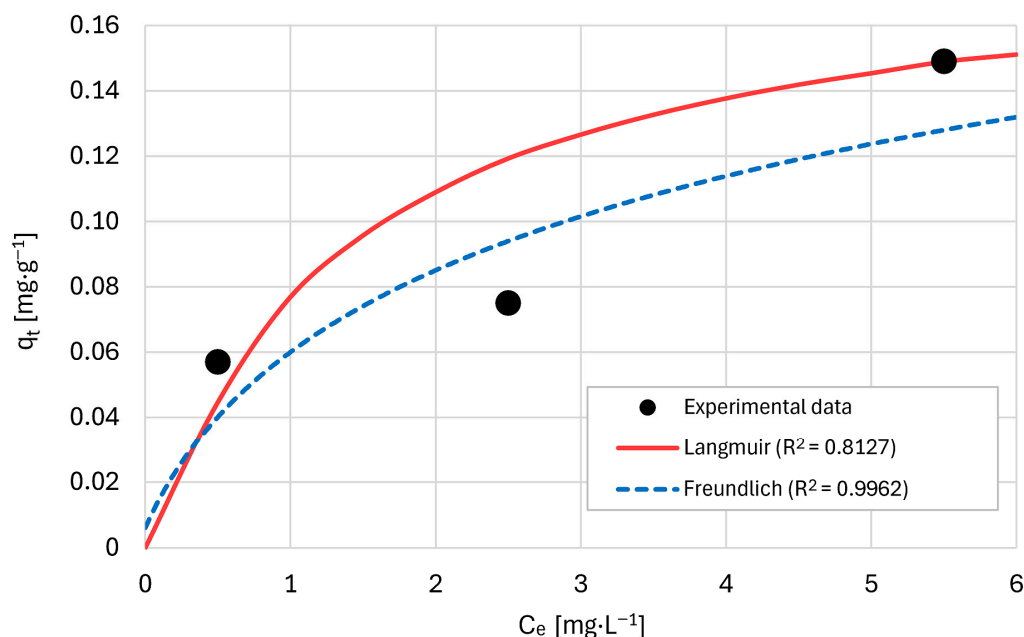


Figure 7. Non-linear fits of the Langmuir and Freundlich isotherms to the equilibrium adsorption experimental data (adsorbent dose = $10.0 \text{ g}\cdot\text{L}^{-1}$).

Table 7. Langmuir and Freundlich isotherm parameters determined by non-linear regression (adsorbent dose = $10.0 \text{ g}\cdot\text{L}^{-1}$).

Isotherm Model	Parameter	Value	Unit
Langmuir	$q_{\max}$	0.187	$\text{mg}\cdot\text{g}^{-1}$
	K_L	0.698	$\text{L}\cdot\text{mg}^{-1}$
	R^2	0.813	—
Freundlich	K_F	0.064	$(\text{mg}\cdot\text{g}^{-1})(\text{L}\cdot\text{mg}^{-1})^{1/n}$
	N	2.477	—
	R^2	0.996	—

The higher R^2 value obtained for the Freundlich model ($R^2 = 0.996$) compared with the Langmuir model ($R^2 = 0.813$) indicates that the Freundlich model better describes the adsorption equilibrium of the system studied. This suggests that adsorption occurs on an energetically heterogeneous surface containing active sites with varying affinity for phosphate ions.

The value of $n = 2.48$ (>1) indicates a favorable adsorption process in the analyzed concentration range and good affinity between the adsorbent and the adsorbate. It should be noted, however, that the Freundlich model is empirical in nature and describes experimental data without providing unambiguous information about the interaction mechanism

between the adsorbent surface and phosphate ions. On the basis of the Langmuir model fit, the theoretical maximum monolayer adsorption capacity ($q_{\max}$) at a dose of $10.0 \text{ g}\cdot\text{L}^{-1}$ was determined to be $0.187 \text{ mg}\cdot\text{g}^{-1}$.

A combined analysis of the kinetic models and adsorption isotherms indicates that the phosphate removal process by 0.25 M CaMLT is complex and involves both surface phenomena and mass transport within the porous structure. The results obtained provide a basis for further studies under dynamic conditions and for a more detailed analysis of the adsorption mechanism using spectroscopic techniques.

3.5. Selection of the Optimal $\text{Ca}(\text{OH})_2$ Modifier Concentration

On the basis of the results presented above, the reactive material obtained by the low-thermal method (MLT) was selected for the modification.

Figure 8 shows the differences in phosphate removal efficacy among the reactive materials modified with the three molar concentrations of $\text{Ca}(\text{OH})_2$ solution. For the initial phosphate concentration of $7 \text{ mg}\cdot\text{L}^{-1}$, the use of 0.1 M CaMLT and 0.25 M CaMLT resulted in a roughly twofold difference in phosphate removal. For example, after 24 h of contact time, removal efficiency was 8% for 0.1 M CaMLT, and 19% for 0.25 M CaMLT. The use of a 0.25 M $\text{Ca}(\text{OH})_2$ solution thus improved phosphate removal efficiency compared with 0.1 M . Increasing the modifier concentration further, to 0.5 M , improved phosphate removal efficiency by approximately 30% compared with the 0.25 M solution.

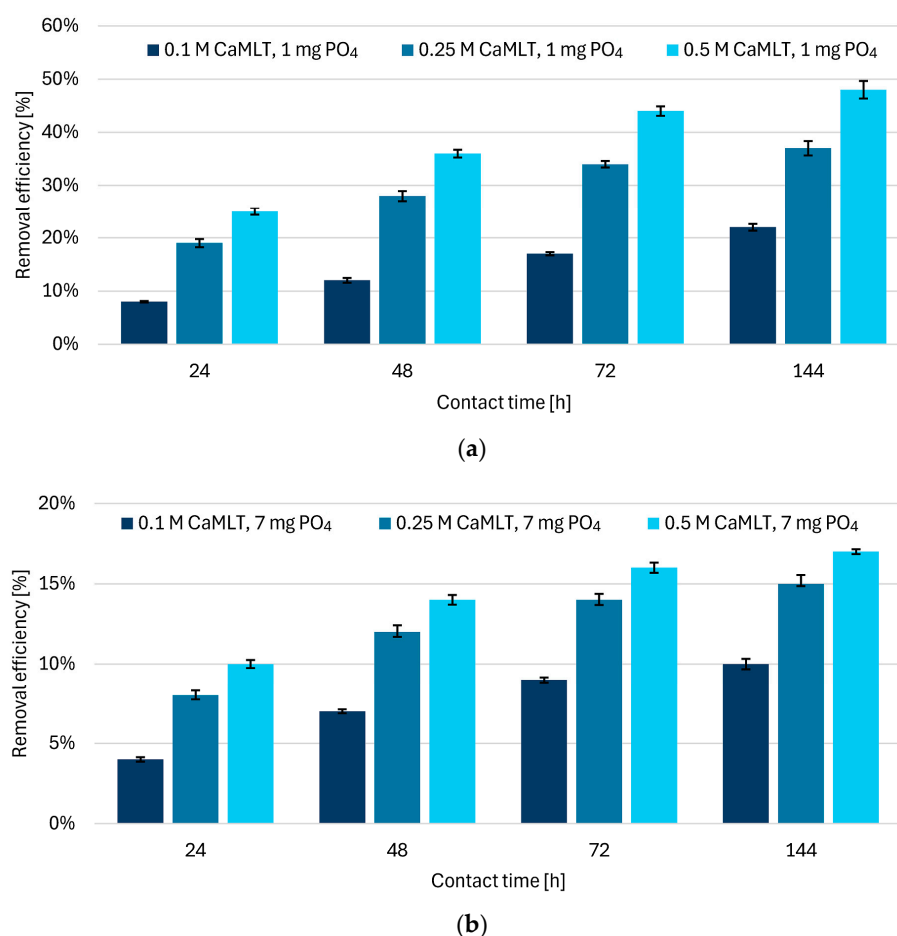


Figure 8. Phosphate removal efficiency as a function of the molar concentration of $\text{Ca}(\text{OH})_2$ used for the modification of the MLT sample. The reported values represent the mean of three replicate determinations. (a) Experimental parameters: $C_i = 1.044 \text{ mg PO}_4\cdot\text{L}^{-1}$; dose = $5.0 \text{ g}\cdot\text{L}^{-1}$; pH = 7.0; time = 24–144 h; (b) Experimental parameters: $C_i = 7.035 \text{ mg PO}_4\cdot\text{L}^{-1}$; dose = $5.0 \text{ g}\cdot\text{L}^{-1}$; pH = 7.0; time = 24–144 h.

For an initial phosphate concentration of $7 \text{ mg}\cdot\text{L}^{-1}$, a comparison of 0.1 M CaMLT and 0.25 M CaMLT again showed higher removal efficiency for 0.25 M CaMLT: after 48 h of contact, removal efficiencies were 7% and 16% for 0.1 M CaMLT and 0.25 M CaMLT, respectively. However, the highest modifier concentration produced only a slight further improvement in removal efficiency; for example, after 72 h, removal efficiency reached 14% for 0.25 M CaMLT and 16% for 0.5 M CaMLT.

The 0.25 M $\text{Ca}(\text{OH})_2$ concentration was therefore selected for further analysis, since no substantial additional improvement was observed for 0.5 M CaMLT.

3.6. Phosphate Removal Efficiency of 0.25 M CaMLT

Phosphate removal efficiency was evaluated on the basis of a series of experiments conducted for the modified reactive material. Figure 9 presents the results obtained for the 0.25 M CaMLT material. Each panel illustrates phosphate removal efficiency as a function of the three material doses applied in the study and the corresponding contact times between the material and the solution. Analysis of the results obtained for 0.25 M CaMLT indicates that, at the lowest phosphate concentration, the maximum removal efficiency reached 56%, attained at the highest material dose and the longest contact time. At a dose of $2.5 \text{ g}\cdot\text{L}^{-1}$, removal efficiency improved markedly—by as much as 10 percentage points—when contact times of 4 and 24 h were compared. For the intermediate dose, removal efficiency increased by 9 percentage points between contact times of 4 and 24 h, and subsequently between 24 and 48 h. At a dose of $10.0 \text{ g}\cdot\text{L}^{-1}$, the corresponding improvements in removal efficiency amounted to 19 and as much as 24 percentage points for the 4–24 h and 24–48 h contact-time intervals, respectively. At higher initial concentrations ($3.277 \text{ mg}\cdot\text{L}^{-1}$ and $7.073 \text{ mg}\cdot\text{L}^{-1}$), removal efficiencies of 23% and 21%, respectively, were achieved at a dose of $10.0 \text{ g}\cdot\text{L}^{-1}$ and a contact time of 144 h.

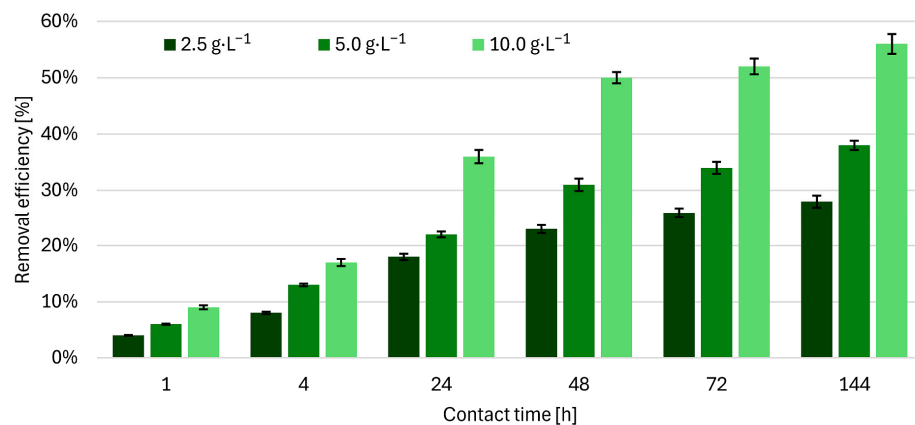
The highest phosphate removal efficiency (56%) was obtained for 0.25 M CaMLT at a dose of $10 \text{ g}\cdot\text{L}^{-1}$ after 144 h of contact, corresponding to an adsorption capacity of $0.057 \text{ mg}\cdot\text{g}^{-1}$ (Table 8). As the initial phosphate concentration increased, adsorption capacity increased to $0.149 \text{ mg}\cdot\text{g}^{-1}$ at $C_i = 7.073 \text{ mg}\cdot\text{L}^{-1}$, despite the lower percentage removal efficiency.

Table 8. Mean adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$) at initial concentrations of (a) $1.021 \text{ mg}\cdot\text{L}^{-1}$, (b) $3.277 \text{ mg}\cdot\text{L}^{-1}$, (c) $7.073 \text{ mg}\cdot\text{L}^{-1}$ by 0.25 M CaMLT (doses 2.5; 5.0; $10.0 \text{ g}\cdot\text{L}^{-1}$) at different contact times.

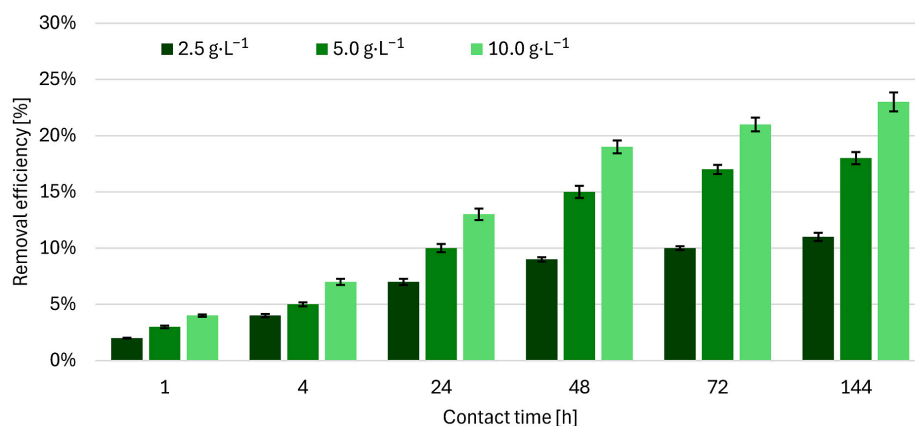
Mean q ($\text{mg}\cdot\text{g}^{-1}$)					
$C_i = 1.021 \text{ mg}\cdot\text{L}^{-1}$					
dose/time	1 h	4 h	24 h	48 h	72 h
$2.5 \text{ g}\cdot\text{L}^{-1}$	0.016	0.033	0.074	0.094	0.106
$5.0 \text{ g}\cdot\text{L}^{-1}$	0.012	0.027	0.045	0.063	0.069
$10.0 \text{ g}\cdot\text{L}^{-1}$	0.009	0.017	0.037	0.051	0.053
$C_i = 3.277 \text{ mg}\cdot\text{L}^{-1}$					
dose/time	1 h	4 h	24 h	48 h	72 h
$2.5 \text{ g}\cdot\text{L}^{-1}$	0.026	0.052	0.092	0.118	0.131
$5.0 \text{ g}\cdot\text{L}^{-1}$	0.020	0.033	0.066	0.098	0.111
$10.0 \text{ g}\cdot\text{L}^{-1}$	0.013	0.023	0.043	0.062	0.069

Table 8. Cont.

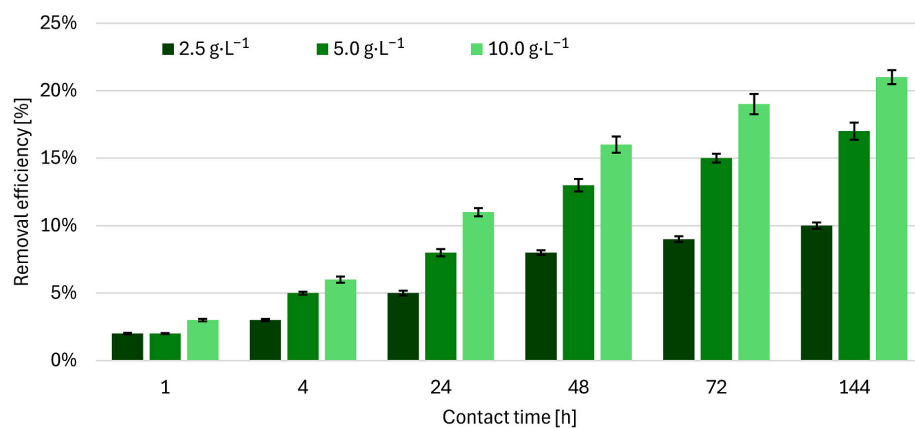
dose/time	Mean q ($\text{mg}\cdot\text{g}^{-1}$)				
	$C_i = 7.073 \text{ mg}\cdot\text{L}^{-1}$				
	1 h	4 h	24 h	48 h	72 h
$2.5 \text{ g}\cdot\text{L}^{-1}$	0.016	0.033	0.074	0.094	0.106
$5.0 \text{ g}\cdot\text{L}^{-1}$	0.012	0.027	0.045	0.063	0.069
$10.0 \text{ g}\cdot\text{L}^{-1}$	0.009	0.017	0.037	0.051	0.053



(a)



(b)



(c)

Figure 9. Phosphate removal efficiency at initial concentrations of (a) $1.021 \text{ mg}\cdot\text{L}^{-1}$, (b) $3.277 \text{ mg}\cdot\text{L}^{-1}$, (c) $7.073 \text{ mg}\cdot\text{L}^{-1}$ by 0.25 M CaMLT (doses 2.5; 5.0; $10.0 \text{ g}\cdot\text{L}^{-1}$) at different contact times.

4. Discussion

The conducted experiments demonstrated that both the synthesis route and the chemical modification of the material influenced its phosphate-removal capacity. The material obtained via the low-temperature method and subsequently modified with calcium hydroxide (0.25 M CaMLT) exhibited the highest phosphate removal efficiency among the materials investigated. These findings indicate that the presence of calcium plays a pivotal role in phosphate-binding processes.

This mechanism is consistent with observations reported by other authors, who demonstrated that calcium-rich materials remove phosphorus through both surface adsorption and the precipitation of sparingly soluble calcium phosphates [11,17,18]. For calcium-modified aluminosilicate materials, the enhancement of phosphate removal efficiency is frequently attributed to an increase in the number of active sorption sites and to the potential formation of stable Ca–P phases [12,23,27].

For the 0.25 M CaMLT material studied, the observed increase in phosphate removal efficiency should be attributed primarily to the presence of calcium phases formed during modification with calcium hydroxide. Calcium may participate in phosphorus immobilization through two complementary mechanisms: (i) specific adsorption (ligand exchange) at the surface of calcium-rich phases, and (ii) precipitation of sparingly soluble calcium phosphates at the material surface. Studies conducted on $\text{Ca}(\text{OH})_2$ – modified clinoptilolite showed that calcium phosphate precipitation and ligand exchange are the dominant mechanisms responsible for phosphate removal, while the contribution of the zeolite framework itself is of secondary importance [27].

Although the results obtained indicate that calcium plays a key role in phosphate removal, it should be noted that the proposed mechanism represents the most probable interpretation and has not been directly verified by spectroscopic methods. The increase in calcium content after material modification, confirmed by XRF analysis, and the clear improvement in phosphate removal efficiency by 0.25 M CaMLT suggest that calcium participates in phosphorus immobilization. This mechanism is consistent with findings reported for calcium-modified aluminosilicate materials, in which both specific adsorption at the surface of calcium phases and surface precipitation of sparingly soluble calcium phosphates have been demonstrated [6,27,45].

It should be emphasized that pH is one of the most important factors influencing phosphate removal, as it determines both phosphate speciation in solution and the solubility of calcium phases and the possibility of calcium phosphate precipitation. In this study, the effect of initial pH (6, 7, and 8) on phosphate removal efficiency was evaluated prior to the main experiments. The results showed only minor differences between the variants analyzed; therefore, pH 7 was adopted for further experiments as a value representative of agricultural drainage waters. The results suggest that within the pH range analyzed, the efficiency of the material remains relatively stable, whereas under more acidic or strongly alkaline conditions the phosphate removal mechanism may change due to shifts in phosphate speciation and the solubility of calcium compounds. This phenomenon has been widely described in the literature on calcium-based materials used for phosphorus removal [3,6].

The observed enhancement in phosphate removal efficiency following $\text{Ca}(\text{OH})_2$ modification confirms the validity of employing simple, low-cost activation methods for aluminosilicate materials. In contrast to numerous advanced adsorbents relying on modification with lanthanum, zirconium, or iron compounds, the use of calcium represents a solution that is more readily implementable and more consistent with the principles of sustainable development [2,18].

The obtained results indicate that phosphate removal efficiency was strongly dependent on contact time, material dose, and initial phosphate concentration. Extension of the

contact time resulted in a gradual increase in removal efficiency, with the highest values recorded after 144 h. This temporal pattern suggests that, in addition to rapid surface adsorption, slower processes such as intraparticle diffusion and the gradual precipitation of calcium phosphates may play a significant role [46].

An increase in material dose led to enhanced phosphate removal efficiency, which can be attributed to the greater availability of active sites and the larger quantity of calcium available to participate in phosphate-binding reactions. Comparable relationships have previously been reported for calcium-based and zeolitic materials applied in the treatment of wastewater and surface water [11,17].

At the same time, an increase in the initial phosphate concentration was accompanied by a decline in percentage removal efficiency. At a PO_4 concentration of $1 \text{ mg}\cdot\text{L}^{-1}$, the 0.25 M CaMLT material achieved a maximum removal efficiency of 56%, whereas at concentrations of 3 and $7 \text{ mg}\cdot\text{L}^{-1}$, removal efficiency decreased to approximately 23% and 21%, respectively. This phenomenon may be attributed to the limited number of available sorption sites and to the progressive saturation of the material surface with phosphorus [2,8].

A comparison of the obtained results with data reported in the literature indicates that the removal efficiency of the 0.25 M CaMLT material falls within the range observed for numerous natural and modified reactive materials applied for phosphorus removal (Table 9). The highest phosphate removal efficiencies are typically achieved by materials enriched with lanthanum, iron, or other specialized additives, for which removal efficiency may exceed 80–99% [47].

It should be noted, however, that direct comparison of phosphate removal efficiencies between different adsorbents should be carried out with caution, as efficiency depends not only on material properties but also on experimental conditions such as initial phosphate concentration, pH, adsorbent dose, contact time, and the chemical composition of the water matrix.

Among modern sorptive materials, some of the highest phosphate removal efficiencies are achieved by layered double hydroxides (LDHs), for which reported sorption capacities frequently exceed $50\text{--}150 \text{ mg P}\cdot\text{g}^{-1}$ and removal efficiency may exceed 90% [48,49]. This high effectiveness results from the presence of positively charged hydroxide layers and an anion exchange mechanism that is not present in conventional aluminosilicate materials.

At the same time, it should be noted that the production of LDH-type materials typically requires multi-step chemical synthesis using highly purified metal salts (Mg, Al, Fe, Zn and Zr), precise pH control, and material aging, which increases production costs and environmental impact. Moreover, many high-performance adsorbents use lanthanum, zirconium, or iron oxide modifications, the application of which may limit the economic viability of large-scale implementation [45].

In contrast, the 0.25 M CaMLT adsorbent developed in the present study was obtained from widely available metakaolin by a low-temperature method and modified exclusively with calcium hydroxide. This approach significantly simplifies the production process, reduces energy consumption, and uses an inexpensive and readily available reagent. Consequently, the practical application potential of the material should be assessed not solely in terms of maximum phosphate removal efficiency, but also with consideration of production costs, raw material availability, ease of implementation, and the overall environmental footprint of the process.

From the perspective of agricultural water treatment systems, reactive materials must not only meet requirements for high sorption efficiency but also be economically justified and applicable in large volumes. In such applications, simplicity of production, material durability, and low unit cost often play as important a role as maximum sorption capacity.

It should be emphasized, however, that the high efficiency of such materials is frequently associated with substantial production costs, the use of expensive reagents, or multi-step synthesis procedures. In contrast, the 0.25 M CaMLT material is based on widely available mineral raw materials and a simple chemical modification process. Its evaluation should therefore be conducted not solely from the perspective of maximum phosphorus removal efficiency, but also with consideration of production costs, raw material availability, and potential environmental impact [11,22,50].

Table 9. Comparison of phosphate removal efficiencies achieved by reactive material.

Material	Type	Removal Efficiency/Capacity	Literature
Natural and modified zeolites	Zeolites	20–90%	[11]
Synthetic zeolites	Zeolites	up to 7 mg P·g ^{−1}	[51]
Zeolites from agro-industrial waste	Waste zeolites	30–80%	[52]
LECA/Filtralite	Lightweight expanded aggregates	20–70%	[10]
Limestone	Calcium material	20–70%	[10]
Apatite	Calcium material	40–90%	[12]
“Opoka” rock/ Polonite®	Calcium material	40–95%	[8]
Crushed concrete	Ca-containing waste material	30–80%	[10]
Fly ash	Waste material	30–90%	[53]
Modified fly ash	Waste material	up to 90%	[13]
Steel slag	Waste material	40–95%	[15]
Modified steel slag	Waste material	>80%	[14]
Biochar	Biochar material	10–60%	[54]
Mg/Ca/Fe-modified biochar	Biochar	60–95%	[55]
Modified biosorbents	Biomaterials	30–80%	[56]
Metal-based adsorbents (Fe, Al, Ca, Mg)	Engineered materials	70–99%	[45]
La-based adsorbents	Engineered materials	80–99%	[57]

Phosphorus is widely recognized as one of the principal factors responsible for the eutrophication of surface waters [11,27,58]. Drainage systems are of particular relevance in this context, as they enable the rapid transport of dissolved reactive phosphorus from agricultural land to watercourses [59,60]. Consequently, the development of technologies enabling phosphorus capture directly within drainage systems is emerging as an important component of water quality protection strategies [59,61,62].

The results obtained in the present study indicate that the 0.25 M CaMLT material may constitute a component of such solutions. Of particular significance is the fact that the material was synthesized using a low-temperature method, which reduces energy consumption relative to conventional zeolite synthesis approaches [22,63,64]. This approach is consistent with the concept of sustainable water treatment and the circular economy, which relies on the utilization of readily available mineral resources and the reduction of the environmental footprint of the production process [10,22].

The significance of calcium-mediated processes extends beyond phosphate removal from water. In recent years, considerable development has been observed in environmental technologies based on controlled calcium compound mineralization. An example is Microbially Induced Calcium Carbonate Precipitation (MICP), which has found application in soil stabilization, erosion control, and improvement of the geotechnical properties of substrates. Wang et al. showed that the application of MICP effectively reduced erosion of granitic residual soils through the formation of calcium carbonate binding soil particles, which increased mechanical strength and resistance to leaching. The authors also emphasized that technologies utilizing calcium-induced mineralization processes represent an environmentally friendly alternative to conventional methods of mineral material stabilization, enabling a reduction in the use of high-carbon-footprint materials and supporting the development of sustainable environmental technologies [65]. Although the mechanism in the present work concerns phosphate immobilization rather than calcium carbonate biomineralization, both processes rely on calcium-induced reactions leading to the stable binding of contaminants or the stabilization of materials. This confirms the broad potential of calcium-based technologies in modern environmental engineering.

An additional advantage lies in the use of metakaolin as a precursor for the reactive material. Kaolin is among the most abundant clay minerals worldwide, and its processing into metakaolin and zeolitic materials is a relatively well-established technological pathway [20,22,66]. Combined with a simple calcium-based modification, this provides a foundation for the development of materials with considerable potential for large-scale implementation.

Reactive materials designed for phosphorus removal are currently considered an integral component of numerous strategies aimed at reducing nutrient emissions from agriculture. On the basis of the properties obtained in the present study, the 0.25 M CaMLT material may be suitable for application in drainage ditches, reactive filters, permeable reactive barriers, and buffer zones [59,61,62,67–70].

A particularly promising direction appears to be the application of the material as a filtration medium in decentralized treatment systems for agricultural drainage water. In such applications, production simplicity, raw material availability, and low operating costs are of comparable importance to phosphorus removal efficiency itself [61,67].

Despite these promising results, several limitations of the present study should be acknowledged. First, the maximum phosphate removal efficiency of 56% remains lower than values reported for certain highly specialized adsorbents [11,50]. Second, attainment of the highest removal efficiency required a relatively long contact time (144 h), which may constrain the applicability of the material under real-world operating conditions [46,70].

It should be emphasized that the results presented were obtained in batch experiments, which represent a standard preliminary assessment stage for new sorptive materials, enabling comparison of their properties under controlled laboratory conditions. The maximum contact time of 144 h applied corresponded to conditions close to sorption equilibrium and was intended to determine the potential phosphate removal capacity of the material, not to replicate actual operating conditions.

In practical agricultural drainage water treatment systems, reactive materials most commonly operate under flow conditions, such as permeable reactive barriers, filter beds, or drainage ditches equipped with sorption inserts. In such applications, phosphorus removal efficiency depends not only on process kinetics but also on hydraulic retention time, flow characteristics, bed geometry, variability of hydraulic loading, and seasonal changes in water chemistry. For this reason, the results of batch experiments should not be directly extrapolated to operating conditions, but should be regarded as a preliminary material screening stage for further research [71].

It should also be noted that in solutions designed to limit phosphorus runoff from agricultural areas, system design is based on providing an appropriate hydraulic retention time and an adequate volume of filtration material, rather than on achieving the sorption equilibrium observed in batch experiments. In practice, considerably shorter contact times are used, the effectiveness of which depends on hydraulic conditions and device design. Therefore, the practical suitability of the developed material should be verified in column experiments conducted under continuous flow conditions using actual drainage waters, which will make it possible to determine the working capacity of the material, its service life, and the influence of competing ions on phosphate removal efficiency. This approach is currently regarded as a necessary stage in the evaluation of reactive materials intended for environmental applications. Furthermore, the experiments were conducted exclusively under batch conditions. However, the performance of reactive materials within drainage systems depends on a range of hydraulic factors, including retention time, flow variability, and the potential for material clogging [67,72]. For this reason, further column-based experiments and field trials are required to evaluate the durability, sorption capacity, and removal efficiency of the material under actual operating conditions [73].

An important aspect of the practical use of reactive materials for phosphate removal is the management of the material after the sorption process has ended. In recent years, increasing attention has been devoted not only to the efficiency of phosphorus removal from water but also to the possibility of its recovery and reuse in accordance with the principles of the circular economy. This approach allows simultaneous limitation of water eutrophication and reduction of agriculture's dependence on non-renewable phosphorite deposits, which are recognized as a critical raw material [74–76].

For calcium-modified adsorbents, phosphates are immobilized primarily through surface adsorption and precipitation of sparingly soluble calcium phosphates. A growing body of research indicates that after the sorption process has ended, two main pathways exist for further management of the material: regeneration of the adsorbent with simultaneous phosphorus recovery, or direct use of the phosphorus-saturated material as a slow-release fertilizer or soil amendment. The latter option is particularly attractive in the case of inexpensive mineral materials for which regeneration may not be economically justified [45,77,78].

Review studies indicate that mineral and calcium-based phosphorus sorbents may, after the end of their service life, serve as a secondary phosphorus source for plants, provided that adequate bioavailability of the bound phosphorus and the environmental safety of the material are confirmed. In this approach, the spent adsorbent ceases to be a waste product and becomes a resource supporting the closure of the phosphorus cycle between the aquatic environment and agricultural production. At the same time, the quantity of waste requiring disposal is reduced, and the demand for fertilizers produced from fossil phosphate resources decreases [45,75,79].

In the case of the 0.25 M CaMLT material developed in this study, the use of metakaolin as a widely available mineral raw material and the application of calcium hydroxide as the sole modifying agent provide favorable premises for further evaluation of post-sorption management options. Given the mineral nature of the material and the phosphate-binding mechanism, it can be assumed that the phosphorus-saturated material could find application as a secondary phosphorus source or as a soil amendment. However, this requires further research encompassing assessment of phosphorus bioavailability for plants, its release kinetics, the chemical stability of the retained phosphates, and the potential presence of contaminants limiting the agricultural use of the material. Such research will make it possible to verify the feasibility of fully integrating the developed material into circular economy strategies and sustainable nutrient management [45,77,79].

5. Conclusions

This study evaluated the phosphate removal efficiency of reactive materials obtained from metakaolin by a low-temperature method and after modification with calcium hydroxide. The results obtained allow the following conclusions to be drawn:

1. Low-temperature synthesis made it possible to obtain a reactive aluminosilicate material based on metakaolin, which is a potentially more energy-efficient alternative to conventional synthesis methods for sorption materials that require high-temperature treatment.
2. Modification of the material with calcium hydroxide significantly increased its ability to remove phosphates, indicating the important role of calcium in phosphate immobilization processes through surface adsorption and the precipitation of poorly soluble phosphate compounds.
3. Kinetic analysis showed that the experimental data are best described by the pseudo-second-order model ($R^2 = 0.977$), while the Weber–Morris model indicated the contribution of both intraparticle diffusion and boundary layer resistance in controlling the rate of the process. Analysis of the adsorption equilibrium showed a very good fit of the Freundlich model ($R^2 = 0.996$), suggesting that adsorption occurs on an energetically heterogeneous material surface. The determined value of the parameter n (>1) indicates a favorable adsorption process in the concentration range studied.
4. Among the analyzed materials, 0.25 M CaMLT (metakaolin after low-temperature synthesis, modified with $\text{Ca}(\text{OH})_2$) showed the highest efficiency, achieving a maximum phosphate removal of 56% at an initial PO_4 concentration of $1.0 \text{ mg}\cdot\text{L}^{-1}$, a material dose of $10.0 \text{ g}\cdot\text{L}^{-1}$, and a contact time of 144 h.
5. Phosphate removal efficiency decreased with increasing initial concentration, which indicates a limited number of available reactive sites and gradual saturation of the material with phosphorus.
6. In addition to the percentage phosphate removal efficiency, the adsorption capacity of the material was also determined. Adsorption capacity increased with increasing initial phosphate concentration, reaching a maximum of $0.149 \text{ mg}\cdot\text{g}^{-1}$, indicating an increase in the amount of phosphorus bound despite the decline in percentage removal efficiency.
7. The developed material combines the advantages of low-temperature synthesis, simple chemical modification, and the use of widely available aluminosilicate raw materials, which increases its potential application as a reactive filter medium in systems for reducing phosphorus runoff from agricultural areas.
8. Although the phosphate removal efficiency obtained was lower than that achieved by some highly modified adsorbents, the material stands out for its simplicity of production, availability of raw materials, and potentially lower energy and environmental costs, which is particularly important for solutions intended for large-scale implementation.
9. Further research should include experiments under flow conditions, assessment of the long-term sorption capacity and regeneration potential of the material, and verification of its performance in real agricultural drainage systems. Actual drainage waters are characterized by considerable seasonal and spatial variability in chemical composition; therefore, the study began with experiments on model solutions, which enabled a reliable comparison of the properties of the materials obtained. Assessment of efficiency in actual drainage waters will constitute the next stage of research, aimed at validating the developed material under operating conditions.

The results obtained indicate that the calcium-modified, low-temperature-synthesized metakaolin-based material may be an element of sustainable strategies for reducing phos-

phorus losses from agricultural areas. The use of materials with lower energy requirements and potential for local production can support efforts to improve surface water quality, reduce eutrophication, and achieve the goals of sustainable water resource management (SDG 6—Clean Water and Sanitation and SDG 15—Life on Land).

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