Article

Comparative Study of Ammonium and Orthophosphate Removal Efficiency with Natural and Modified Clay-Based Materials, for Sustainable Management of Eutrophic Water Bodies

Irene Biliani [ID], Vasiliki Tsavatopoulou [ID] and Ierotheos Zacharias *[ID]

Laboratory of Environmental Engineering, Department of Civil Engineering, University of Patras,
26504 Patras, Greece; biliani.i@ac.upatras.gr (I.B.); vasoutsav@gmail.com (V.T.)
* Correspondence: izachari@upatras.gr

Abstract: Eutrophication, a global threat that leads to degradation of freshwater and seawater aquatic ecosystems, is driven by excessive nutrient loading. This study explores the sustainable management of eutrophic water bodies with the application of natural and modified clay-based materials as a practical solution to mitigate eutrophication by removing ammonium and orthophosphate ions. Comparative analyses of six materials: natural zeolite, bentonite, and perlite, along with their modification with calcium and iron, were assessed after kinetic analysis of each material. Batch adsorption experiments were performed to evaluate the material's performance in fresh and seawater. Fitting experimental data assessed adsorption kinetics to pseudo-second-order models. Furthermore, Langmuir isotherm models were employed to determine each material's maximum adsorption capacity for ammonium and orthophosphate ion uptake. The results revealed that freshwater applications of modified zeolite or natural bentonite achieved better orthophosphate ion removal efficiency from seawater, whereas employing natural zeolite maximized the ammonium ion removal efficiency in freshwater bodies. Finally, orthophosphate and ammonium ion removal efficiency results for almost all materials were diminished in seawater. This research contributes valuable insights to the development of efficient and sustainable nutrient removal methodologies to remediate natural eutrophic water bodies and protect aquatic ecosystems.

Keywords: ammonium ions; orthophosphate ions; zeolite; bentonite; perlite; modifications; coastal; freshwater; adsorption; removal efficiency; sustainability; management; capacity

1. Introduction

Eutrophication, a pressing and significant threat to freshwater ecosystems globally, is primarily driven by the excessive influx of nutrients, particularly ammonium (NH_4^+) and orthophosphate (PO_4^{3-}), into aquatic environments. These nutrients, originating from agricultural runoff, wastewater discharge, and industrial activities, stimulate algal blooms, disrupt aquatic food webs, and ultimately lead to oxygen depletion, threatening aquatic life and ecosystem health. Consequently, mitigating eutrophication and controlling nutrient pollution in freshwater bodies have become critical environmental imperatives, underscoring the importance of this research.

Among the various remediation strategies, chemical adsorption has emerged for nutrient control due to its cost-effectiveness [1,2], operational simplicity, and minimal environmental impact [3]. Clay-based materials, including natural and modified clays, have garnered significant attention as potential adsorbents for nutrient elimination due to their abundant availability, increased surface area, and inherent ion exchange capabilities. There is an extensive scientific literature that employs the application of zeolites [3–6], bentonites [7–10] and perlite [11–13] for water purification approaches When a clay-based material is applied as a slurry to treat eutrophication by controlling nutrients in the water, this material ends up in the benthic environment. This deposited clay-based material

effectively mitigates the released sediment nutrient fluxes, due to sediments' phosphate legacy [14–16], by re-adsorbing nitrogen and phosphorus and hence providing long-term eutrophication control.

Zeolites, characterized by their porous aluminosilicate structure, exhibit excellent cation exchange capacity, making them highly effective for ammonium adsorption [17,18]. Zeolites are crystalline hydrated aluminosilicates containing sodium, potassium, and calcium whose lattice structure is negatively charged [19]. The charge is balanced by cations ($\pm$Ba, $\pm$Sr, and $\pm$Mg) with a three-dimensional framework that may exchange with cations in aquatic reagents [20]. The natural material of zeolite is capable of high ion exchange capacity, and its shape-selective structures function as molecular sieves. They allow the passage of substances of a specific size, which is why they are classified according to their size [19]. Through ion exchange, zeolite achieves removal of nitrogen by ammonium adsorption, which releases calcium ions that trigger phosphate ions [21]. Incorporating inorganic materials into natural zeolite aims to amplify the adsorption capacity and to ameliorate the physicochemical characteristics of the natural zeolite, like high specific surface area, porosity, and thermal stability [22]. Such modifications include the compositions of natural zeolites with $Ca(OH)_2$ [23],„Al–Mn binary oxide [24], NaOH and $AlCl_3$ [25], and many others.

Bentonite is a rock that consists mainly of the montmorillonite clay mineral Al_2O_3. $4SiO_2$. vH_2O (in a percentage greater than 80%), formed by altering acidic volcanic rocks. When the content of montmorillonite is lower (60–80%), the material is characterized as "bentonite clay". Bentonite, a phyllosilicate clay [26] with a high surface area and swelling capacity, demonstrates a strong affinity for phosphate adsorption due to its surface hydroxyl groups [27]. Owing to its net negative charge, it is an excellent adsorbent for metal and organic cations, but it is a poor sequester of phosphate [28]. Therefore, bentonite's physical and chemical modifications aim to make it more receptive to adsorbing phosphorus. Such modifications frequently comprise multiple inorganic substances, like the modification of bentonite with $Mg(OH)_2$ [29], with $CaCO_3$ [28], with Mg-doped biochar/bentonite composite [30], and many others.

Perlite is a white, acidic, volcanic, glassy rock of rhyolite composition (rich in SiO_2), formed by the sudden cooling and solidification of volcanic lava, trapping water in its mass. Perlite, an amorphous volcanic glass, possesses a porous structure [11], and its modification aims to improve its adsorption capacity for both ammonium and orthophosphate [17,27,31]. The granules of expanded perlite are inert [32]. Perlite is a porous material with adsorption properties, but it has not yet been extensively studied for the adsorption of phosphorus and ammonia. A recent work presents a compound of perlite with nano-Fe/Ce and with nano-Fe alone to assess their phosphate removal [13].

While numerous studies have investigated the individual adsorption capacities of zeolite, bentonite, and perlite for nutrient removal, comparative studies evaluating the performance of these materials, both in their natural and modified forms, are limited. Furthermore, understanding the characteristics of adsorption through kinetic and isotherm experiments is crucial for optimizing the design and operation of effective treatment systems.

This study aims to comprehensively analyze ammonium and orthophosphate removal efficiencies using three natural clay-based materials—zeolite, bentonite, and perlite—and their modified counterparts. The research will focus on evaluating the adsorption kinetics of ammonium and orthophosphate onto each material through batch experiments, determining the rate-limiting steps and adsorption mechanisms, determining the adsorption isotherm parameters for each material, providing insights into the maximum adsorption capacity and affinity for ammonium and orthophosphate, and comparing the performance of natural and modified clay-based materials, assessing the impact of modification on nutrient removal efficiency.

This research provides valuable insights into the potential of utilizing clay-based materials for mitigating eutrophication in freshwater ecosystems. The findings aid in

developing efficient and sustainable nutrient removal technologies for the remediation of polluted water bodies.

2. Materials and Methods

Laboratory study of natural zeolite, bentonite, perlite and modified zeolite, bentonite and perlite has been carried out to compare the optimal phosphorus and nitrogen removal efficiency.

2.1. Origin of Materials

Zeocem company (from Bystré, Slovakia) supplied natural zeolite; its granulometry was 0.6–1.8 mm. Its chemical composition contains 65.1% SiO_2, 12.9% Al_2O_3, 1.2% Na_2O, 1.6 K_2O, 3% CaO, 1.5% MgO, 1.5% FeO and 12.9% H_2O. Natural bentonite was supplied by Prolat company.(from Athens, Greece) Its composition comprises 64.63% SiO_2, 13.70% Al_2O_3, 2.72% Fe_2O_3, 3.94% CaO, 2.26% MgO, K_2O 0.16% and Na_2O 2.32%. Perlite was obtained from ISOCON (from Athens, Greece). Before use, all materials were sieved at final granulometry of 0.15 nm and washed three times with deionized water. Afterward, the materials were dried at 105 °C for 24 h.

2.2. Preparation of the Modified Materials

Generally, several metals, including iron (Fe) and calcium (Ca), have been examined to inactivate P. If iron is used, in that case, additional aeration is required so that the iron oxides formed are sensitive to redox and can release P under limited oxygen conditions [33]. Iron (Fe)-based materials have demonstrated the potential to efficiently remove phosphorus in treating eutrophic lakes [34], while the ecosystem health is preserved since iron particles do not harm plankton and benthic organisms found in the aquatic ecosystem [35]. Also, calcium was added to clay-based materials. Calcium can be used with different clays, especially zeolite, to remove ammonium from water through ion exchange processes [36]. The calcium ions can replace the ammonium ions in the zeolite structure, effectively removing contaminants [37].

The modification includes two stages. During the first one, 200 mL of 0.1 M $CaCl_2$ (solid: liquid = 1:43 *w/w*) was poured in 10 g of the adsorbent material and stirred for 4 h. The procedure was repeated two more times. The modified material was stirred with 200 mL of deionized water for 10 min. The process was repeated three times, and then the mixture was placed in an oven at 80 °C for 24 h to remove the humidity of the material produced. Afterward, 10 g of precipitate was immersed into 200 mL of 0.1 M $FeCl_3$ $6H_2O$ (solid:liquid = 1:36 *w/w*) and stirred for 5 h. The process was repeated two times. Finally, the modified material was stirred in 200 mL of deionized water for 10 min. The process was repeated three times, and then the mixture was placed in an oven at 80 °C for 24 h. Further details of the preparation procedure for the materials are presented in the schematic diagram of Figure 1.
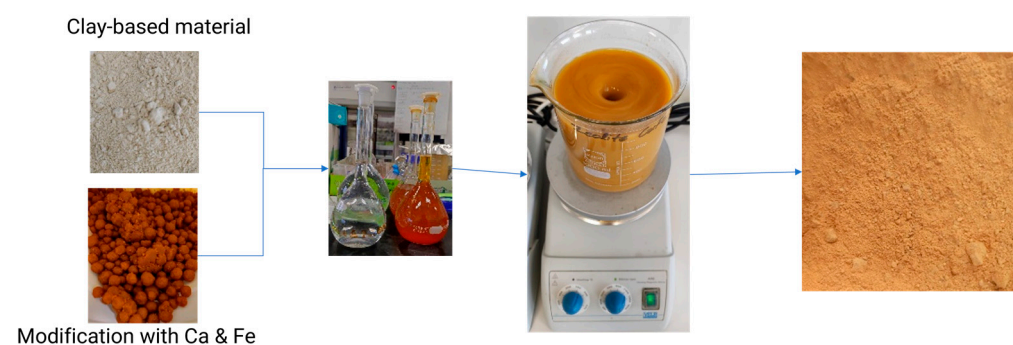

Clay-based material

Modification with Ca & Fe

Figure 1. Schematic diagram of preparation of the modified clay-based materials.

The modified materials had the following chemical compositions: for modified zeolite, 31.71% O, 3.96% Na, 13.07% Al, 33.33% Si, 0.65% K, 5.56% Ca, 11.73% Fe; for modified bentonite: 28.99% O, 5.6% Al, 29.22% Si, 0.85 K, 23.14% Fe, 12.2% Ca; and for modified perlite: 34.4% O, 1.2% Na, 7.19% Al, 30.77% Si, 0.88% K, 13.08% Ca and 12.23% Fe.

2.3. Kinetic Adsorption

The adsorption kinetics and mechanisms governing the removal of ammonium and orthophosphate ions using clay-based materials have been extensively studied [38]. These models can give important insight into reaction rates and the sorption mechanism. They contain information about diffusion, mass transfer, and reactions on the adsorbent's surface during adsorption. Many kinetic models have been evaluated when assessing how well-varied materials work, such as zeolite, bentonite, and perlite (natural and modified). Pseudo-second-order kinetic models are commonly used to characterize the behavior of the adsorption process, because they offer valuable information on the rate-limiting phases and the whole adsorption process [39]. Also, the pseudo-second-order model [40] indicates a chemisorption-dominated mechanism.

The performance of the materials in this study, including zeolite, bentonite, and perlite (both natural and modified), was evaluated using a variety of kinetic models. Notably, the pseudo-second-order kinetic model resulted in a higher R^2 of up to 99%. The pseudo-second-order kinetic model can be expressed as follows in Equation (1) [41]:

$$\frac{dq_t}{dt} = k_2 (Q_e - Q_t)^2 \qquad (1)$$

where the parameter k_2 (g/(min mg)) represents the rate constant of the pseudo-second-order kinetic model, and Q_t and Q_e describe the quantity of nutrients adsorbed onto the material surface at time 't' and at the 'equilibrium (e)' state, respectively [41]:

The linearized-integrated form of Equation (1) is the following Equation (2):

$$\frac{t}{Q_t} = \frac{1}{k_2 q Q_e^2} + \frac{t}{Q_e} \qquad (2)$$

where the parameters k_2 and Q_e are calculated from the intercept and slope of the trendline resulting from the plot of 't/Q_t' against 't'.

Kinetic adsorption experiments were performed on all the different materials. More specifically, natural zeolite, bentonite and perlite, modified zeolite with $CaCl_2$ and $FeCl_3$ $6H_2O$ (zeolite CaFe), modified bentonite with $CaCl_2$ and $FeCl_3$ $6H_2O$ (bentonite CaFe), modified perlite with $CaCl_2$ and $FeCl_3$ $6H_2O$ (perlite CaFe) were tested for their capacity to adsorb orthophosphates (PO_4^{3-}) and ammonium ions (NH_4^+) (Table 1).

At first, two 2 L volumetric flasks were prepared containing 0.1 mg/L of orthophosphates (PO_4^{3-}-P) and 1 mg/L of ammonium ions (NH_4^+-N). Two salinities were examined: 0‰ (freshwater) and 35‰ (seawater). The experiments simulated the conditions prevailing in the Aitoliko lagoon. Subsequently, 100 mL of the initial solution of ammonium ions (1 mg/L) and a quantity of the corresponding material were put in the Erlenmeyer flask (250 mL) to obtain the desired concentration of the adsorbent. The exact process was also followed for orthophosphates, where the Erlenmeyer flask (250 mL) contained 150 mL of the initial blank solution (0.1 mg/L). The examined concentration of each adsorbent was 100 mg/L. Sampling was performed nine times using the method of filtration: 0, 15 min, 30 min, 1 h, 2 h, 4 h, 8 h, 10 h, and 24 h. The experiment was carried out at an ambient temperature of 25 ± 1 °C at neutral pH = 7 and was repeated twice.

Table 1. Pseudo-second-order results for ammonium and orthophosphate ion removal efficiency of natural and modified materials, using 1 mg NH_4^+-N/L and 0.1 mg PO_4^{3-}-P/L initial concentrations.

Pollutant	Material	Q_e mg/g	k_2 g/(min × mg)	R^2
NH_4^+	N-zeolite	8.59	0.10	0.9963
	N-bentonite	6.33	0.10	0.9998
	N-perlite	5.30	0.79	0.9075
	Mod-zeolite	5.63	0.002	0.9941
	Mod-bentonite	4.61	0.013	0.9992
	Mod-perlite	4.81	0.001	0.7431
PO_4^{-3}	N-zeolite	0.53	0.07	0.999
	N-bentonite	1.00	0.016	0.937
	N-perlite	0.28	0.009	0.555
	Mod-zeolite	0.95	0.046	0.9995
	Mod-bentonite	0.88	0.039	0.9994
	Mod-perlite	0.24	0.093	0.9231

2.4. Adsorption Isotherms

The adsorption isotherm presents the equilibrium relationship between the concentration in the solution and the concentration in the adsorbent particles at a given temperature and pressure [42]. The concentration of the substance adsorbed on the clay (Q_e) is expressed as the mass adsorbed per unit mass of the initial clay-based material that has units in mg/g. The equilibrium adsorption behavior is typically described by the Langmuir model, which assumes monolayer adsorption on a homogeneous surface [43]. Table 2 of this study presents the experimental results using the well-known Langmuir adsorption isotherm model.

Table 2. Langmuir isotherm results for 0.1 g/L of adsorbent material in 100 mL of sampling volume for 0–100 mg NH_4^+-N/L and 0–10 mg PO_4^{3-}-P/L pollutants.

Pollutant	Material	Q_m mg/g	k_L L/mg	R^2
NH_4^+	N-zeolite	5.52	0.39	0.9997
	N-bentonite	6.43	0.08	0.9739
	Mod-zeolite	7.90	0.09	0.9106
	Mod-bentonite	2.12	0.01	0.98399
PO_4^{-3}	N-zeolite	0.68	0.05	0.99
	N-bentonite	0.92	0.00	0.9984
	Mod-zeolite	0.24	0.43	0.9978
	Mod-bentonite	0.18	0.26	0.9665

Monolayer sorption on discrete selective adsorption sites implies uniform energies of monolayer sorption onto the sorbent surface and shows no transmigration of the adsorbate in the plane of the surfaces [41]. The linear description of the Langmuir isotherm is expressed as Equation (3) [44]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \tag{3}$$

where 'C_e' is the concentration of the solution at equilibrium state (mg/L), 'Q_e' is the amount of nutrient sorbed at equilibrium state, 'K_L' is the Langmuir sorption constant (L/mg) at a given temperature, related to the energy of sorption, 'Q_m' is the maximum sorption capacity (mg/g). The Langmuir isotherm model can also be expressed as Equation (4) [45]:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{4}$$

A dimensionless constant or separation factor (R_L) is expressed as Equation (5) [46]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

where 'R_L' is used to describe the favorable nature of the adsorption process, where $R_L > 1$ is unfavorable, $R_L = 0$ is linear, $0 < R_L < 1$ is favorable, and $R_L = 0$ is irreversible [46,47]. The plot of '$1/Q_e$' against '$1/C_e$' produces a straight-line graph with the values of 'Q_m' and 'K_L' calculated from the slope and intercept, respectively.

For the experiments of isothermal simultaneous adsorption of ammonia and orthophosphate ions using natural and modified materials, a quantity of corresponding material equal to 0.1 g was used. The material was added to 100 mL of orthophosphate and ammonia ion solution of different initial concentrations of 0.1, 0.5, 1, 5, 10 mg PO_4^{3-}/L and 1, 5, 10, 50, and 100 mg NH_4^+/L, respectively. The mixtures were then agitated (25 °C, 200 rpm, 24 h), allowing the adsorption to reach equilibrium. After 24 h, the suspensions were filtered (0.45 μm membrane) to determine PO_4^{3-}-P by ascorbic acid and indophenol blue, respectively. Each experiment was conducted at pH 7.0 and repeated three times.

2.5. Experimental Procedures

The residual concentration of orthophosphates and ammonia ions in the respective solutions was assessed spectrophotometrically by ascorbic acid and indophenol blue, respectively, after 24 h. More specifically, orthophosphates were determined by the ascorbic acid method after digestion of the sample with ammonium persulfate [48]. The absorbance was measured at 880 nm with a spectrophotometer (U-1100, Hitachi, Tokyo, Japan) [49]. Ammonia reacts with hypochlorite, phenol, and sodium nitroprusside, forming a bright blue complex. The absorbance was measured at 640 nm with a spectrophotometer (U-1100, Hitachi, Tokyo, Japan) [50]. The initial ratio of the pollutant's concentration was 10 to 1 for N to P to simulate realistic conditions of eutrophic coastal freshwater bodies [51]. Both kinetic and isotherm experiments lasted 24 h, during which the temperature was maintained at 25 °C and the pH 7; therefore, no assimilation in ammonia results was expected [52].

The software Grammarly (v 1.2.113.1522) was used for English editing.

3. Results

3.1. Ammonium Ion Uptake by Natural Materials in Seawater and Freshwater

Figure 2 shows the concentration of the ammonium ion adsorption on the N-zeolite, N-bentonite, and N-perlite against time. The adsorption capacity results for these clays follow the Langmuir model, and the kinetic results can be described using the pseudo-second model fitting. The results demonstrate that N-zeolite had higher ammonium ion adsorption capacity (Q_e = 8 mg/g) than the other natural materials after 240 min of treatment for both seawater and freshwater (Figure 2(a1)). N-bentonite's ammonium ion adsorption capacity differs for seawater and freshwater, in which its adsorption capacity reached 4 and 6 mg/g (Figure 2(a2)). In contrast, the adsorption capacity of N-perlite was up to 3 mg/g for seawater and freshwater (Figure 2(a3)). The removal efficiency results demonstrate that the N-zeolite and N-bentonite presented almost double, if not higher, removal efficiency for ammonium ions compared to N-perlite. In particular, the percentage of ammonium ion adsorption was 80–60%, 60–40%, and 30–10% for N-zeolite, N-bentonite, and N-perlite in freshwater and seawater after 24 h of treatment (Figure 2(c1–c3)). The results indicate that N-zeolite is favored as an ammonium ion adsorbent in both seawater and freshwater compared to the other clay-based materials.
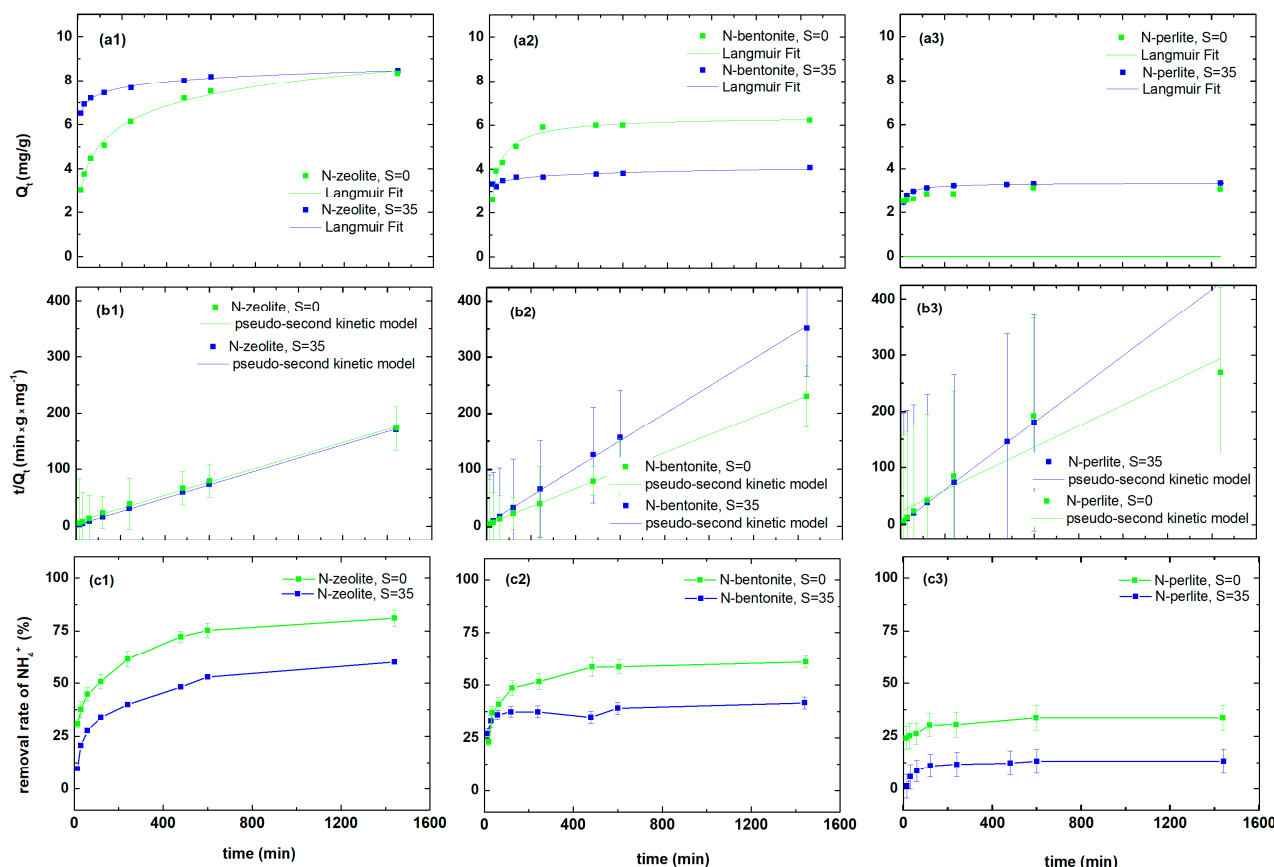
Figure 2. (**a**) Langmuir fitting results for ammonium ion adsorption by (**a1**) N- zeolite, (**a2**) N-bentonite, and (**a3**) N-perlite; (**b**) pseudo-second-order kinetics of ammonium uptake by (**b1**) N-zeolite, (**b2**) N-bentonite, and (**b3**) N-perlite; (**c**) ammonium removal rate (%) of (**c1**) N-zeolite, (**c2**) N-bentonite, and (**c3**) N-perlite. The adsorption capacity was evaluated for freshwater (S = 0, results shown in green) and seawater (S = 35‰, results shown in blue) in a 1 mg NH_4^+-N/L pollutant solution.

3.2. Orthophosphate Ion Uptake by Natural Materials in Seawater and Freshwater

Figure 3 shows the concentrations of orthophosphate ions adsorbed on N-zeolite, N-bentonite, and N-perlite over time. The adsorption capacity results for these clays follow the Langmuir model, and the kinetic results can be described using the pseudo-second model fitting. It is observed that the orthophosphate ion adsorption took up to 600 min, where the orthophosphate ion adsorption capacity reached up to Q_e = 0.6 and 0.4 mg/g for N-zeolite (Figure 3(a1)) in freshwater and seawater accordingly. N-bentonite's orthophosphate ion adsorption capacity reached up to 0.9 mg/g for both seawater and freshwater (Figure 3(a2)). In contrast, the adsorption capacity of N-perlite was up to 0.2 mg/g for seawater and freshwater (Figure 3(a3)). In general, it is found that the adsorption results for 0.1 mg PO_4^{3-}-P/L were delayed by 140 min or about 2 h compared to the adsorption results for ammonium ion uptake of 1 mg NH_4^+-N/L (Figure 3(a1–a3)). The pseudo-second fitting model can successfully describe the modified zeolite and modified bentonite (Figure 3(b1,b2)) but fails to represent the modified perlite (Figure 3(b3)) adequately. The removal efficiency results demonstrate that the N-zeolite and N-bentonite can also efficiently adsorb orthophosphate ions in the waterbodies. Finally, the percentage of orthophosphate ion adsorption was 60%, 85%, and 20% for N-zeolite, N-bentonite, and N-perlite in freshwater and seawater after 24 h of treatment (Figure 3(c1–c3)). The results indicate that N-bentonite is favored for orthophosphate ion adsorbance in both seawater and freshwater compared to the other clay-based materials.
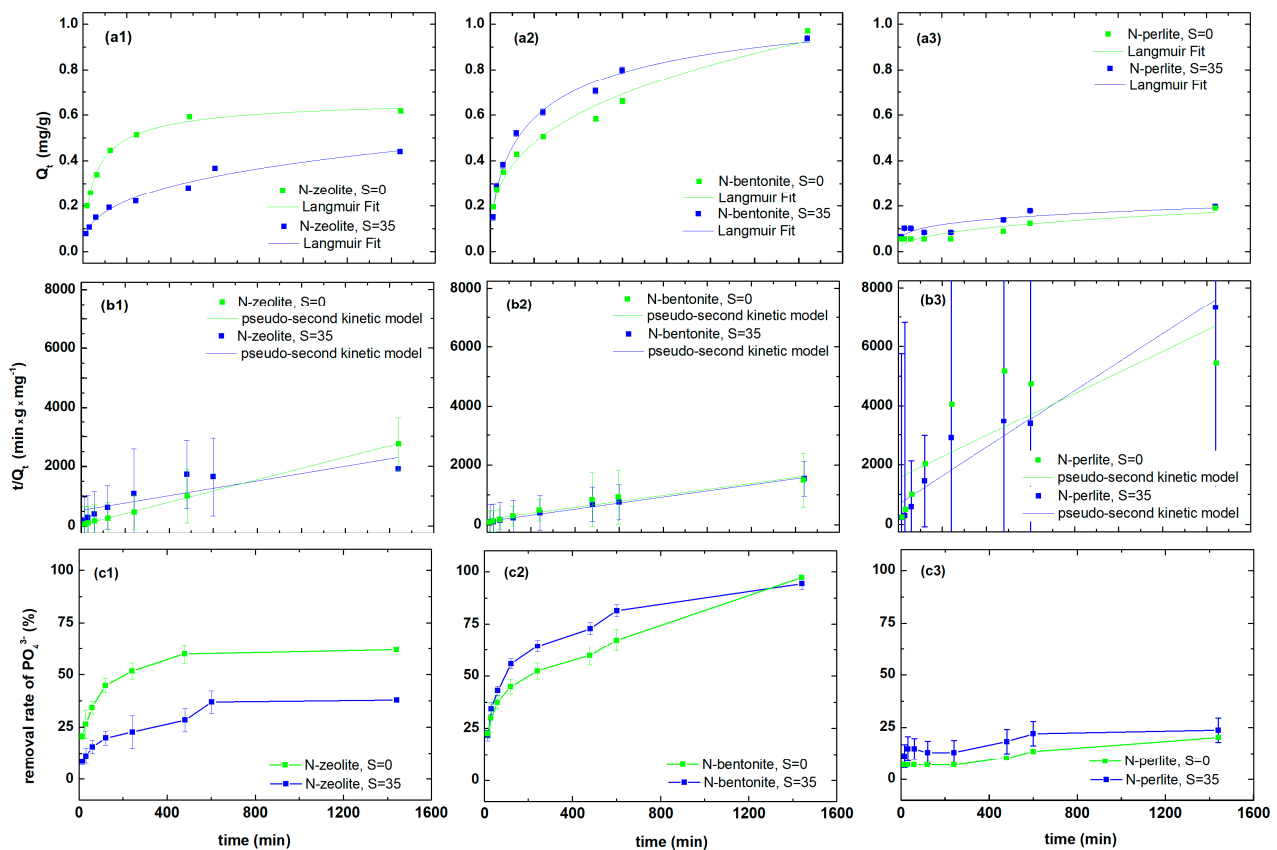
Figure 3. (**a**) Langmuir fitting results for orthophosphate ion adsorption by (**a1**) N-zeolite, (**a2**) N-bentonite, and (**a3**) N-perlite; (**b**) pseudo-second-order kinetics of orthophosphate uptake by (**b1**) N-zeolite, (**b2**) N-bentonite, and (**b3**) N-perlite; (**c**) orthophosphate removal rate (%) of (**c1**) N-zeolite (**c2**) N-bentonite, and (**c3**) N-perlite. The adsorption capacity was evaluated for freshwater (S = 0, results shown in green) and seawater (S = 35‰, results shown in blue) in a 0.1 mg $PO_4{}^{3-}$-P/L pollutant solution.

3.3. Ammonium Ion Uptake by Modified Materials in Seawater and Freshwater

Figure 4 shows the concentrations of ammonium ions adsorbed on the modified zeolite, modified bentonite, and modified perlite over time. The adsorption capacity results for the above modified clays follow the Langmuir model, and the kinetic results can be described using the pseudo-second model fitting. It is observed that most adsorption took up to 240 min, similarly to the results using the natural clays for ammonium ion adsorbance (Figure 2). In particular, the ammonium ion adsorption capacity was up to Q_e = 5 and 4 mg/g for modified zeolite in freshwater and seawater (Figure 4(a1)). Modified bentonite's ammonium ion adsorption capacity did not differ significantly for seawater and freshwater, reaching up to 4 mg/g accordingly (Figure 4(b1)). In contrast, the adsorption capacity of modified perlite was up to 3 and 4 mg/g for seawater and freshwater (Figure 4(c1)). The pseudo-second fitting model can successfully describe the modified zeolite and modified bentonite (Figure 4(b1,b2)) but fails to adequately represent the modified perlite (Figure 4(b3)). Modified zeolite's ammonium removal efficiency decreased for freshwater applications and remained the same for seawater applications compared to N zeolite's ammonium ion adsorbent efficiency results (Figure 2(c1)). The same results were obtained for the ammonium ion adsorbance efficiency of modified bentonite (Figure 2(c2)) and modified perlite (Figure 2(c3)). In addition, the modification described in Section 2.2. for ammonium ion uptake favors zeolite application (Figure 4(c1–c3)).
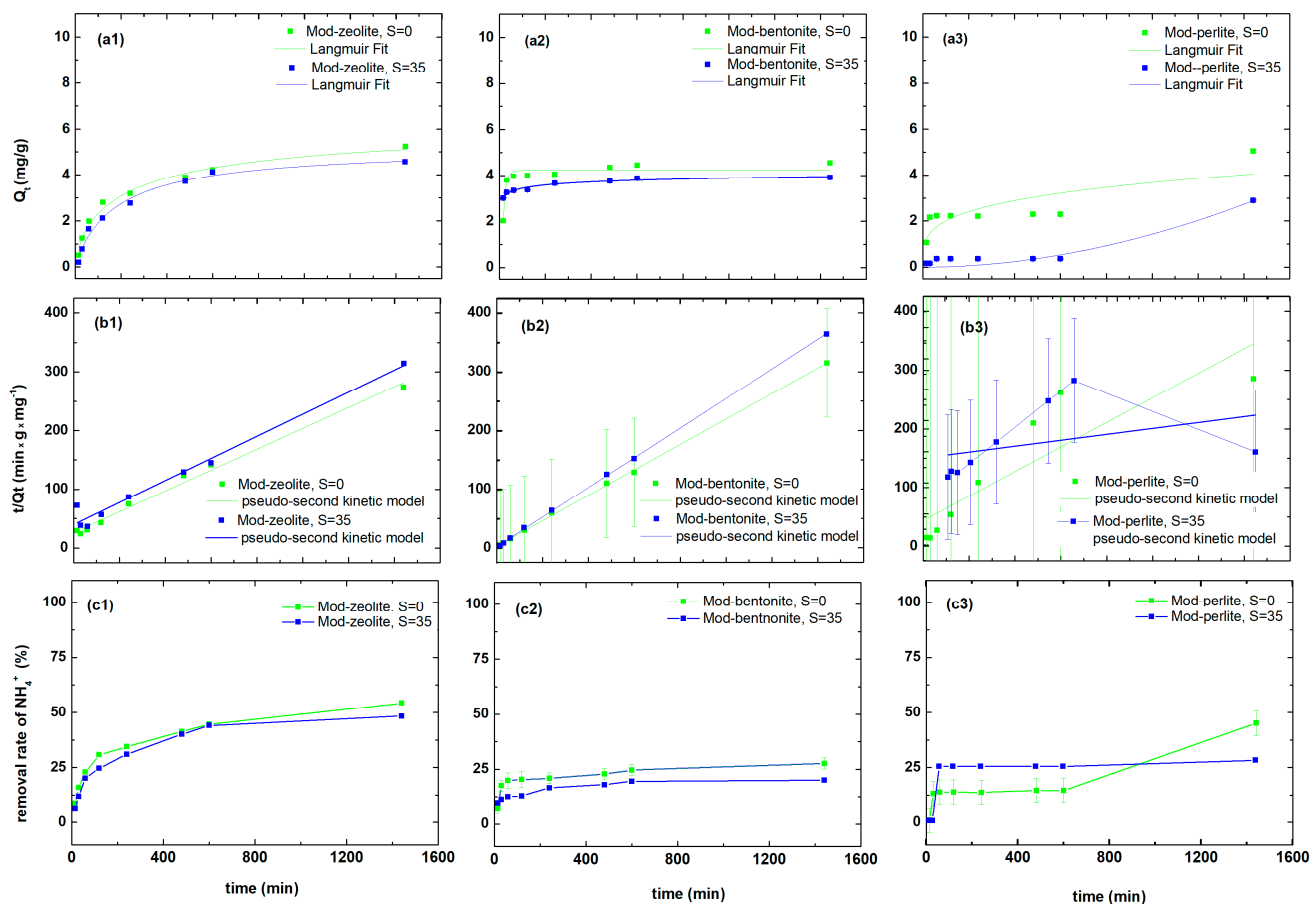
Figure 4. (**a**) Langmuir fitting results for ammonium ion adsorption by (**a1**) modified zeolite, (**a2**) mod-bentonite, and (**a3**) modified perlite; (**b**) pseudo-second-order kinetics of ammonium-uptake by (**b1**) modified zeolite, (**b2**) modified bentonite, and (**b3**) modified perlite; (**c**) ammonium removal rate (%) of (**c1**) modified zeolite, (**c2**) modified bentonite, and (**c3**) modified perlite. The adsorption capacity was evaluated for freshwater (S = 0, results shown in green) and seawater (S = 35‰, results shown in blue) in a 1 mg NH_4^+-N/L pollutant solution.

3.4. Orthophosphate Ion Uptake by Modified Materials in Seawater and Freshwater

Figure 5 shows the concentrations of orthophosphate ions adsorbed on the modified zeolite, modified bentonite, and modified perlite over time. The adsorption capacity results for the above modified clays follow the Langmuir model, and the kinetic results can be described using the pseudo-second model fitting. It is observed that most adsorptions took up to 600 min, similarly to the results using natural clays for orthophosphate ion adsorbance (Figure 3). In particular, the orthophosphate ion adsorption capacity was up to Q_e = 0.9 and 0.8 mg/g for modified zeolite in freshwater and seawater. Modified bentonite's orthophosphate ion adsorption capacity did not differ significantly for seawater and freshwater, reaching up to 0.85 mg/g accordingly. In contrast, the adsorption capacity of modified perlite was up to 0.05 and 0.2 mg/g for seawater and freshwater. Modified zeolite's orthophosphate removal efficiency reached up to 90 and 75% for freshwater and seawater applications (Figure 5(c1)). Modified bentonite's orthophosphate removal efficiency reached up to 80 and 75% for freshwater and seawater applications (Figure 5(c2)). Modified perlite's orthophosphate removal efficiency reached 35 and 25% for freshwater and seawater applications (Figure 5(c3)). The modified materials showed significantly increased uptake of orthophosphate ions compared to the natural materials' adsorption removal efficiency (Figure 3(c1–c3)).
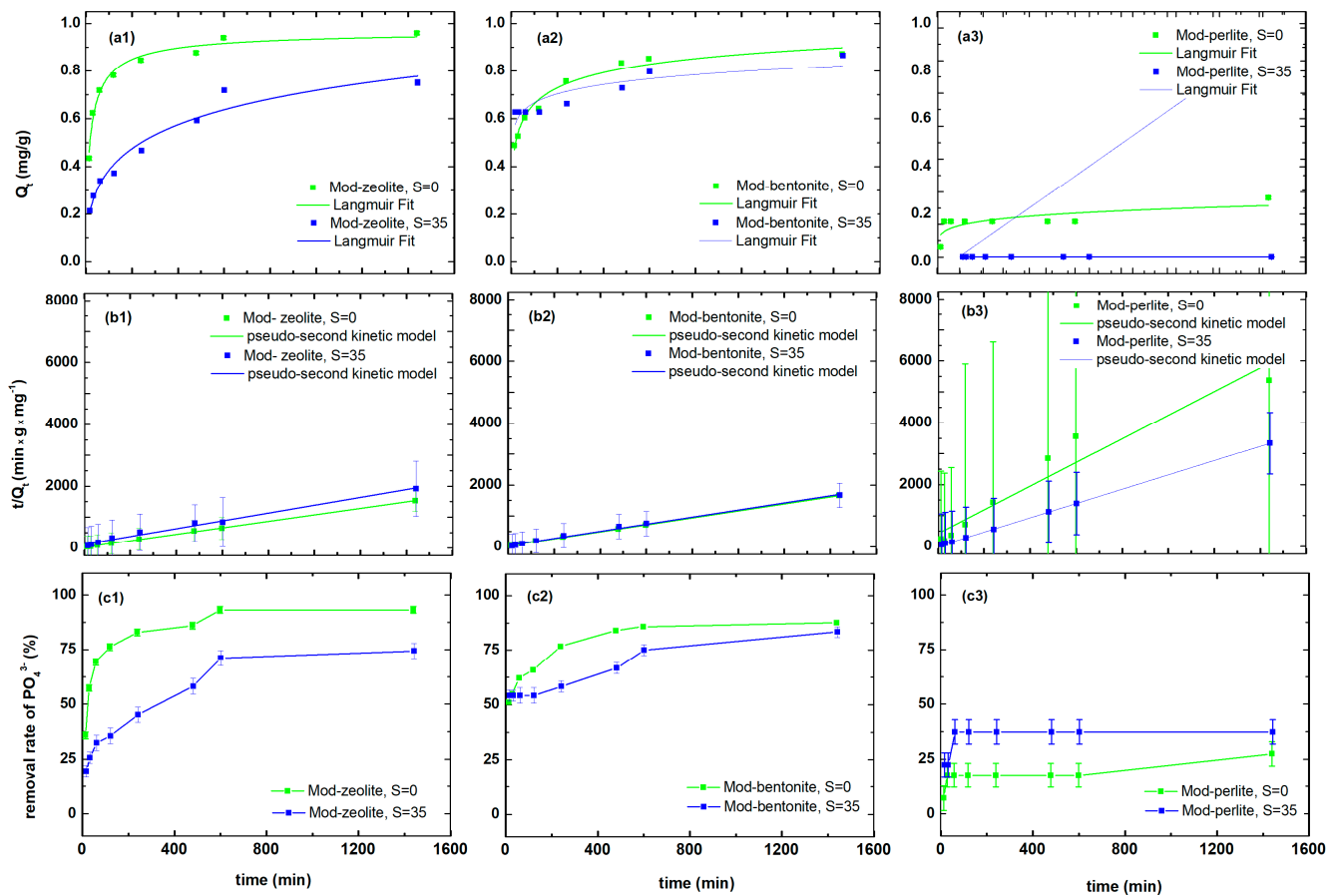
Figure 5. (**a**) Langmuir fitting results for orthophosphate ion adsorption by (**a1**) modified zeolite, (**a2**) modified bentonite, and (**a3**) modified perlite; (**b**) pseudo-second-order kinetics of orthophosphate uptake by (**b1**) modified zeolite, (**b2**) modified bentonite, and (**b3**) modified perlite; (**c**) orthophosphate removal rate (%) of (**c1**) modified zeolite, (**c2**) modified bentonite, and (**c3**) modified perlite. The adsorption capacity was evaluated for freshwater (S = 0, results shown in green) and seawater (S = 35‰, results shown in blue) in a 0.1 mg PO_4^{3-}-P/L pollutant solution.

3.5. Ammonium Isotherm Results

Figure 6 depicts the NH_4^+ removal rate (%) as a function of time (0.25–24 h) for natural materials, as well as the amount of ammonia ions removed from the solution per unit mass of natural minerals over a 24-hour period, as a function of the residual solute, for various initial ammonia ion concentrations (1, 5, 10, 50, and 100 mg/L). Analytically, the proportion of materials removed was 81% and 60.5% for N-zeolite and N-bentonite, respectively. Figure 6 (right) depicts the association between the amount of ammonium ions extracted from the solution per unit of material and the initial concentration of ammonium ions in the solution. The typical Langmuir model fits nicely. For N-bentonite, adsorption had not yet achieved a plateau, and the residual concentration at the conclusion of our experiment, i.e., 24 h, was C_e = 50 mg/L. The curve for N-zeolite appeared to reach a plateau of about C_e = 10 mg/L, with Q_{max} = 5 mg/mg. Modified zeolite provided 45.6%, respectively, followed by modified bentonite at 27.6%. The data have been simulated using the Langmuir model. The yield with modified zeolite was higher than that with the other materials, and ammonium absorption increased substantially when the equilibrium concentration rose from 0 to 10 mg/L, eventually plateauing at 50 mg/L. The Q_e value after 24 h was 5.5 mg/g. Modified bentonite had a corresponding Q_e value of 2 mg/g. Modified bentonite plateaued at 25 mg/L, whereas modified zeolite plateaued at 20 mg/L.
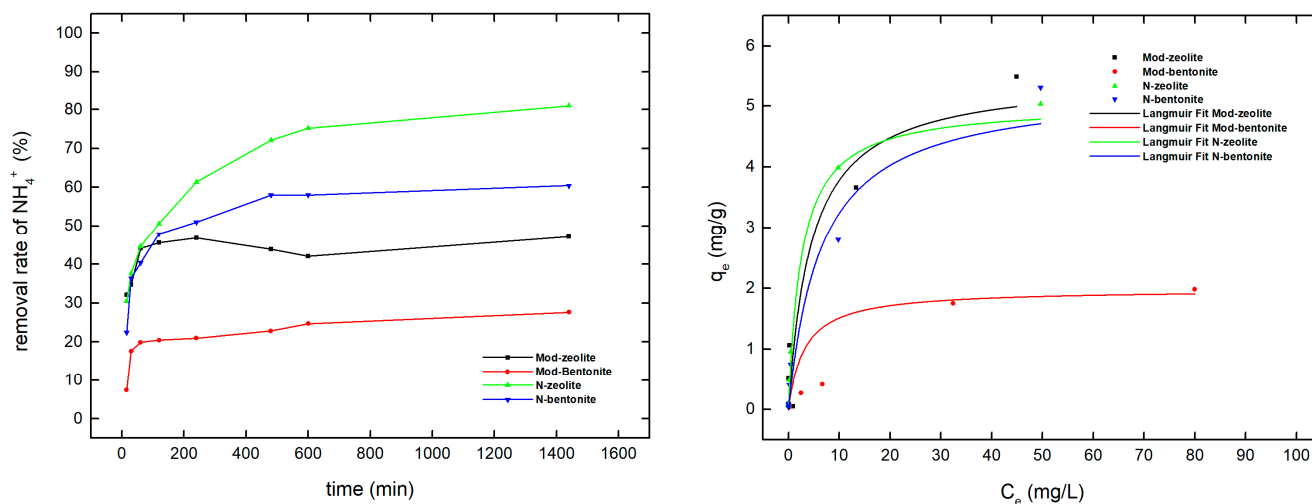
Figure 6. Removal of ammonium ions from aqueous solution with initial ammonium ion concentration of 1 mg/L and 0.01 g of adsorbent materials, pH = 7, T = 25 °C (**left**). Adsorption isotherms for ammonium ions using natural zeolite, natural bentonite, modified zeolite and modified bentonite in combined aqueous solutions. The quantity of the adsorbent materials was 0.01 g, pH = 7, T = 25 °C (**right**).

3.6. Orthophosphate Isotherm Results

Figure 7 depicts the phosphate removal efficiency of natural materials with time (0.25–24 h). More precisely, N-bentonite had the highest performance, reaching 97% efficiency; second in line was N-zeolite, with a removal rate of around 62%, for a percentage of 20%. Figure 7 illustrates the equilibrium connection between the adsorption capacity of natural zeolite and bentonite and the starting concentration of orthophosphate ions in the solution. A 0.01 g amount of each mineral was added to 100 mL of orthophosphate ion solution with starting concentrations of 0.1, 0.5, 1, 5, and 10 mg PO_4^{3-}/L. The data have been simulated using the Langmuir model. The findings show that N-bentonite's adsorbance capacity for orthophosphate ions was larger than that of the other two natural materials, suggesting that it had not yet plateaued. The representative Q_e value for N-zeolite was 0.082 mg/g, whereas the Q_e value after 24 h was 0.16 mg/g. Therefore, the usage of N-bentonite is advantageous for high orthophosphate concentrations in aquatic environments. In terms of orthophosphates, the clearance rate for modified zeolite was 93% and for modified bentonite, 88% It matches quite well with the standard Langmuir model. Since the modified bentonite appeared not to have yet reached its plateau, its image was far superior to that of the other two materials. After a 24-hour period, the representative Q_e for modified zeolite was 0.17 mg/g, but the value for modified bentonite was 0.54 mg/g.
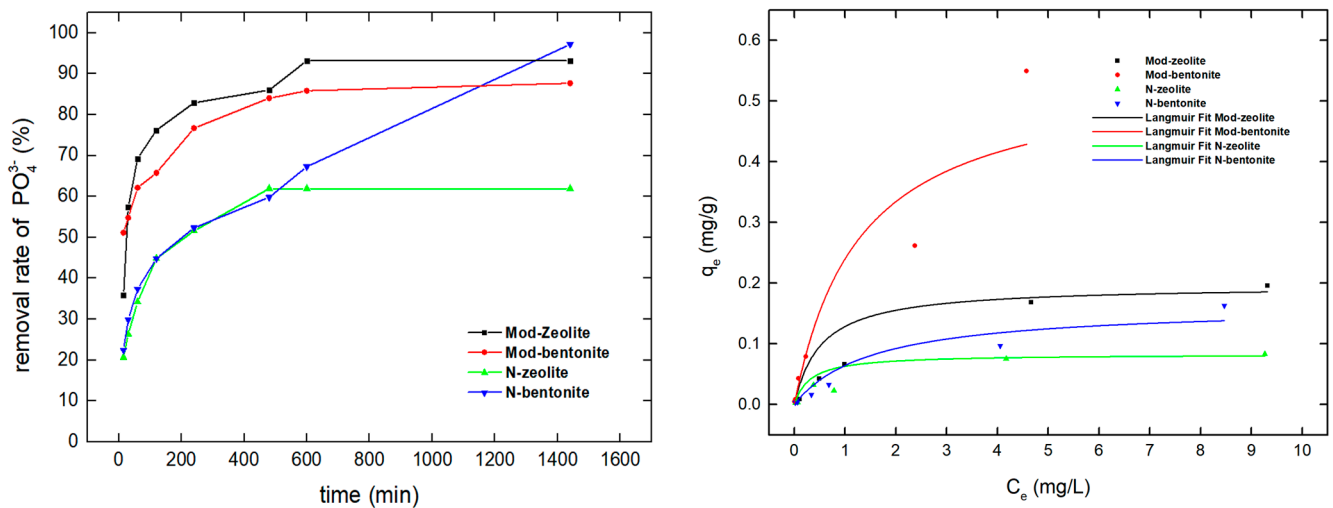
Figure 7. Removal of orthophosphate ions from aqueous solution with initial orthophosphate ion concentration of 0.1 mg/L and 0.01 g of adsorbent materials, pH = 7, T = 25 °C (**left**). Adsorption isotherms for orthophosphate ions using natural zeolite, natural bentonite, modified zeolite and modified bentonite in combined aqueous solutions. The quantity of the adsorbent materials was 0.01 g, pH = 7, T = 25 °C (**right**).

4. Discussion

The purpose of the research was to examine the use of natural materials (zeolite, perlite, bentonite) to remove phosphate and ammonia ions from eutrophic waters. Natural clays have offered compelling advantages for eutrophication control practices since (1) they are abundant in nature and cost-effective [53], (2) their application is ecological and sustainable [4], and (3) they present high adsorbance capacity in nutrient control [54]. This study reviews their application in natural and modified forms to assess their adsorbance efficiency for mitigation of eutrophic water bodies.

The residence time of sorbate uptake at the solid–solution interface can be identified through kinetics, which can also reveal details about adsorption mechanisms. The materials examined follow the pseudo-second kinetic order that suggests reactions of more chemical affinity, which might include the electron-sharing process, electron exchange, surface complexation, and internal diffusion [55]. The Langmuir model is a satisfactory fit for all materials in terms of adsorption. Monolayer adsorption onto the adsorbent's finite and identical surfaces is assumed by the Langmuir isotherm [56]. Also, the isotherm is associated with the equilibrium concentration of a solute on the surface of an adsorbent with the solute's concentration in the liquid at a specific temperature. Zeolite-based materials in their natural or modified form are widely known for their ability to remove phosphate and ammonium ions from eutrophic water bodies because of their distinct microporous architectures, large surface areas, ion exchange capabilities, and environmental benefits [57]. On the other hand, bentonite constitutes a valuable mineral, owning to its remarkable physicochemical properties, flexible crystalline and chemical structure, excellent surface area, environmental value, high ion replacement, high absorption capabilities, and high natural availability [55]. These data were verified by the results of our experiments, as analyzed below.

The experiments were performed for 100 mg/L of material in aqueous solution for different salinity conditions, S = 0‰ and S = 35‰. The efficiency in removing phosphates and ammonium ions in S = 35‰ was lower for almost all tested materials, natural and modified, due to the competition that occurs between the ions that are present in coastal waters [58]. In contrast to ortho-phosphate adsorption efficiency (65% and 40% for fresh and coastal waters, respectively), natural zeolite exhibits a greater ammonium adsorption efficiency (75% for fresh and 60% for coastal waters), according to the study's findings. However, the ammonium removal efficiency (nearly 50% for fresh and coastal waters) was

lower than the orthophosphate removal efficiency (90 and 75% for fresh and coastal waters) of the calcium and iron-modified zeolite. Similarly, orthophosphate ions are more easily removed by the modified zeolite containing iron oxide [59] than ammonium ions.

The kinetic results indicated that in freshwater, the removal efficiency of ammonium ions is optimized by applying natural zeolite. In contrast, in seawater, natural and modified zeolite applications achieved similar results. In contrast, applying natural bentonite or modified zeolite in freshwater achieved higher orthophosphate ion removal efficiency. The most outstanding adsorbent removal efficiency for orthophosphate ions was found in seawater after applying natural bentonite.

Table 1 presents the kinetic characteristics of the pseudo-second-order model for all materials that were assessed in this study. The results reveal that pseudo-second-order models can effectively describe the kinetic characteristics of zeolite and bentonite, concluding that the adsorption mechanism is governed by ion exchange and therefore by the chemical adsorption process [51]. Other modifications of clay-based materials, such as the modified bentonite, named Bephos [60], clearly showed enhanced ammonium and phosphorus adsorption capacity in freshwaters compared to coastal waters. The comparison between the pseudo-second-order kinetic results for the natural clay-based materials show that natural zeolite yields higher ammonium adsorbance capacity than natural bentonite, as shown by Fan et al. [51].

In addition, the results from adsorption kinetics indicate that most materials achieved their optimum performance after 10 h in the orthophosphate ion solutions and after 8 h in the ammonium ion solutions. This indicates that a significant portion of the adsorption capacity is reached in a comparatively short time, indicating that the adsorption of these ions follows a relatively rapid kinetic process.

Table 2 presents the isotherm results of the Langmuir model for the best four materials in terms of higher removal efficiency (N-zeolite, N-bentonite, Mod-zeolite, Mod-bentonite). The results reveal that the Langmuir model can effectively describe the adsorbance capacity of these four materials.

Table 2 depicts that natural clay-based materials present higher adsorbance capacity for ammonium than for orthophosphate, as shown by Fan et al. [51]. The isotherm results reveal that introducing calcium and iron on zeolite leads to increased ammonium ion adsorbance capacity (from 5.52 to 7.90 mg/g) and decreased orthophosphate ion adsorbance capacity (from 0.68 to 0.18 mg/g) the treatment dose was 10 mg per 100 mL of sampling volume containing from 0 to 100 mg NH^{4+}-N/L and 0 to 10 mgPO_4^{3-}-P/L. Other modified materials, such as the modified bentonite of Bephos [16], exhibit higher adsorption capacity for orthophosphate than for ammonium. Clay-based materials, unlike certain other adsorbents like chlorella vulgaris [61], are effective even in seawater environments where phosphate removal may be hampered by ion competition [28,62]. Also, in comparison to certain biochar materials, clay-based material applications are not restricted by acid pH levels [54,55]. Other clay-based modifications, such as Lanthanum-modified zeolites (LMZ) [63], presented clear advantages in ammonium adsorption capacity compared to other widely used clays such as 'Phoslock', but due to the complexity of extraction, Lanthanum-based modifications are more expensive than many other metals, such as iron or aluminum [64]. Natural clays, as ready-to-use materials, are cost-efficient and do not present unforeseen environmental risk. Since natural clays are found in many aquatic environments, there are no unforeseen ecological threats for the ecosystems such as with other clay-based materials using organic compounds such as kaolinite combined with carica papaya seeds and metal doping [65].

5. Conclusions

Clay-based materials have been proven to be very promising materials in the restoration of eutrophic water bodies through chemical adsorption. This application allows phosphate and ammonium ions to be effectively removed from polluted natural waters

after an inexpensive, quick, simple, effective, and eco-friendly action, despite the fact that several adsorbents have been used over time.

The results of the study indicate that natural zeolite presents higher adsorption efficiency for ammonium (75% and 60% for fresh and coastal waters, respectively) than for orthophosphate (65% and 40% for fresh and coastal waters, respectively). However, the zeolite modified with calcium and iron had higher removal efficiency for orthophosphate (90% and 75% for fresh and coastal waters) than for ammonium (almost 50% for fresh and coastal waters).

A comparison of the pseudo-second-order kinetic findings for the natural clay-based materials revealed that natural zeolite has a ammonium adsorbance capacity than natural bentonite. Significant research has been conducted, and various measures are proposed to treat eutrophication. Scientific research is necessary to ensure the correct restoration methodology. As we concluded from the previous chapter, there is no single method of recovery. Each natural water body is unique and governed by different climatic conditions, interdependencies, and the organisms that live or act in it [66]. Choosing the right restoration methods and defining specific actions are essential for achieving sustainable, ecologically sound, and cost-effective water ecosystem recovery.

References

1. Dotto, G.L.; McKay, G. Current Scenario and Challenges in Adsorption for Water Treatment. *J. Environ. Chem. Eng.* **2020**, *8*, 103988. [CrossRef]
2. Gupta, G.; Khan, J.; Singh, N.K. Application and Efficacy of Low-Cost Adsorbents for Metal Removal from Contaminated Water: A Review. *Mater. Today Proc.* **2021**, *43*, 2958–2964. [CrossRef]
3. Duan, P.; Ding, S.; Jiao, L.; Wang, M.; Zhang, Y.; Qian, C. Simultaneous Immobilization of Ammonia and Phosphorous by Thermally Treated Sediment Co-Modified with Hydrophilic Organic Matter and Zeolite. *J. Environ. Manag.* **2023**, *339*, 117800. [CrossRef] [PubMed]
4. Senila, M.; Cadar, O. Modification of Natural Zeolites and Their Applications for Heavy Metal Removal from Polluted Environments: Challenges, Recent Advances, and Perspectives. *Heliyon* **2024**, *10*, e25303. [CrossRef] [PubMed]
5. Wu, Y.; Song, L.; Shi, M.; Gu, C.; Zhang, J.; Lv, J.; Xuan, L. Ca/Fe-Layered Double Hydroxide–Zeolite Composites for the Control of Phosphorus Pollution in Sediments: Performance, Mechanisms, and Microbial Community Response. *Chem. Eng. J.* **2022**, *450*, 138277. [CrossRef]
6. Han, M.; Wang, Y.; Zhan, Y.; Lin, J.; Bai, X.; Zhang, Z. Efficiency and Mechanism for the Control of Phosphorus Release from Sediment by the Combined Use of Hydrous Ferric Oxide, Calcite and Zeolite as a Geo-Engineering Tool. *Chem. Eng. J.* **2022**, *428*, 131360. [CrossRef]

7. Kang, L.; Haasler, S.; Mucci, M.; Korving, L.; Dugulan, A.I.; Prot, T.; Waajen, G.; Lürling, M. Comparison of Dredging, Lanthanum-Modified Bentonite, Aluminium-Modified Zeolite, and FeCl2 in Controlling Internal Nutrient Loading. *Water Res.* **2023**, *244*, 120391. [CrossRef]

8. Xu, H.; Hu, X.; Chen, Y.; Li, Y.; Zhang, R.; Tang, C. Xi Hu Cd(II) and Pb(II) Absorbed on Humic Acid-Iron-Pillared Bentonite: Kinetics, Thermodynamics and Mechanism of Adsorption. *Colloids Surfaces A Physicochem. Eng. Asp.* **2020**, *612*. [CrossRef]

9. Zhan, Q.; Teurlincx, S.; van Herpen, F.; Raman, N.V.; Lürling, M.; Waajen, G.; de Senerpont Domis, L.N. Towards Climate-Robust Water Quality Management: Testing the Efficacy of Different Eutrophication Control Measures during a Heatwave in an Urban Canal. *Sci. Total Environ.* **2022**, *828*, 154421. [CrossRef]

10. Han, Y.; Jeppesen, E.; Lürling, M.; Zhang, Y.; Ma, T.; Li, W.; Chen, K.; Li, K. Combining Lanthanum-Modified Bentonite (LMB) and Submerged Macrophytes Alleviates Water Quality Deterioration in the Presence of Omni-Benthivorous Fish. *J. Environ. Manag.* **2022**, *314*, 115036. [CrossRef]

11. Baie, M.S.; Esfandian, H.; Nesheli, A.A. Removal of Nitrate from Aqueous Solutions in Batch Systems Using Activated Perlite: An Application of Response Surface Methodology. *Asia-Pac. J. Chem. Eng.* **2016**, *11*, 437–447. [CrossRef]

12. Sari, A.; Tuzen, M.; Citak, D.; Soylak, M. Adsorption Characteristics of Cu(II) and Pb(II) onto Expanded Perlite from Aqueous Solution. *J. Hazard. Mater.* **2007**, *148*, 387–394. [CrossRef] [PubMed]

13. Guo, B.; Fan, C.; Meng, J.; Yang, Y. The Comparative Study of a Nano-Fe0-Loaded and a Nano-Fe/Ce-Loaded Expanded-Perlite on Removal of Phosphate from Water. *J. Water Process Eng.* **2023**, *56*, 104336. [CrossRef]

14. Spears, B.M.; Lürling, M.; Yasseri, S.; Castro-Castellon, A.T.; Gibbs, M.; Meis, S.; McDonald, C.; McIntosh, J.; Sleep, D.; Van Oosterhout, F. Lake Responses Following Lanthanum-Modified Bentonite Clay (Phoslock®) Application: An Analysis of Water Column Lanthanum Data from 16 Case Study Lakes. *Water Res.* **2013**, *47*, 5930–5942. [CrossRef] [PubMed]

15. Lin, Q.; Zhang, K.; Shen, J.; Liu, E. Integrating Long-Term Dynamics of Ecosystem Services into Restoration and Management of Large Shallow Lakes. *Sci. Total Environ.* **2019**, *671*, 66–75. [CrossRef] [PubMed]

16. Zamparas, M.; Drosos, M.; Deligiannakis, Y.; Zacharias, I. Eutrophication Control Using a Novel Bentonite Humic-Acid Composite Material Bephos™. *J. Environ. Chem. Eng.* **2015**, *3*, 3030–3036. [CrossRef]

17. Trujillo-Reyes, J.; Peralta-Videa, J.R.; Gardea-Torresdey, J.L. Supported and Unsupported Nanomaterials for Water and Soil Remediation: Are They a Useful Solution for Worldwide Pollution? *J. Hazard. Mater.* **2014**, *280*, 487–503. [CrossRef] [PubMed]

18. Wang, S.; Peng, Y. Natural Zeolites as Effective Adsorbents in Water and Wastewater Treatment. *Chem. Eng. J.* **2010**, *156*, 11–24. [CrossRef]

19. De Velasco-Maldonado, P.S.; Hernández-Montoya, V.; Montes-Morán, M.A.; Vázquez, N.A.R.; Pérez-Cruz, M.A. Surface Modification of a Natural Zeolite by Treatment with Cold Oxygen Plasma: Characterization and Application in Water Treatment. *Appl. Surf. Sci.* **2018**, *434*, 1193–1199. [CrossRef]

20. Dizadji, N.; Dehpouri, S.; Vossoughi, S.S.S. Experimental Investigation of Adsorption of Heavy Metals (Copper (II)) from Industrial Wastewater with Clinoptilolite. *Chem. Eng. Trans.* **2012**, *29*, 1309–1314. [CrossRef]

21. Wan, C.; Ding, S.; Zhang, C.; Tan, X.; Zou, W.; Liu, X.; Yang, X. Simultaneous Recovery of Nitrogen and Phosphorus from Sludge Fermentation Liquid by Zeolite Adsorption: Mechanism and Application. *Sep. Purif. Technol.* **2017**, *180*, 1–12. [CrossRef]

22. Roshanfekr Rad, L.; Anbia, M. Zeolite-Based Composites for the Adsorption of Toxic Matters from Water: A Review. *J. Environ. Chem. Eng.* **2021**, *9*, 106088. [CrossRef]

23. Mitrogiannis, D.; Psychoyou, M.; Koukouzas, N.; Tsoukalas, N.; Palles, D.; Kamitsos, E.; Pantazidis, A.; Oikonomou, G.; Baziotis, I. Phosphate Recovery from Real Fresh Urine by Ca(OH)2 Treated Natural Zeolite. *Chem. Eng. J.* **2018**, *347*, 618–630. [CrossRef]

24. Wu, K.; Li, Y.; Liu, T.; Zhang, N.; Wang, M.; Yang, S.; Wang, W.; Jin, P. Evaluation of the Adsorption of Ammonium-Nitrogen and Phosphate on a Granular Composite Adsorbent Derived from Zeolite. *Environ. Sci. Pollut. Res.* **2019**, *26*, 17632–17643. [CrossRef] [PubMed]

25. Zhang, H.; Lyu, T.; Liu, L.; Hu, Z.; Chen, J.; Su, B.; Yu, J.; Pan, G. Exploring a Multifunctional Geoengineering Material for Eutrophication Remediation: Simultaneously Control Internal Nutrient Load and Tackle Hypoxia. *Chem. Eng. J.* **2021**, *406*, 127206. [CrossRef]

26. Kasprzyk, M.; Gajewska, M. Phosphorus Removal by Application of Natural and Semi-Natural Materials for Possible Recovery According to Assumptions of Circular Economy and Closed Circuit of P. *Sci. Total Environ.* **2019**, *650*, 249–256. [CrossRef]

27. Khan, S.A.; Khan, T.A. Clay-Hydrogel Nanocomposites for Adsorptive Amputation of Environmental Contaminants from Aqueous Phase: A Review. *J. Environ. Chem. Eng.* **2021**, *9*, 105575. [CrossRef]

28. Perassi, I.; Borgnino, L. Adsorption and Surface Precipitation of Phosphate onto $CaCO_3$-Montmorillonite: Effect of PH, Ionic Strength and Competition with Humic Acid. *Geoderma* **2014**, *232–234*, 600–608. [CrossRef]

29. El Bouraie, M.; Masoud, A.A. Adsorption of Phosphate Ions from Aqueous Solution by Modified Bentonite with Magnesium Hydroxide $Mg(OH)_2$. *Appl. Clay Sci.* **2017**, *140*, 157–164. [CrossRef]

30. Xi, H.; Zhang, X.; Hua Zhang, A.; Guo, F.; Yang, Y.; Lu, Z.; Ying, G.; Zhang, J. Concurrent Removal of Phosphate and Ammonium from Wastewater for Utilization Using Mg-Doped Biochar/Bentonite Composite Beads. *Sep. Purif. Technol.* **2021**, *285*, 120399. [CrossRef]

31. Shah, G.M.; Nasir, M.; Imran, M.; Bakhat, H.F.; Rabbani, F.; Sajjad, M.; Farooq, A.B.U.; Ahmad, S.; Song, L. Biosorption Potential of Natural, Pyrolysed and Acid-Assisted Pyrolysed Sugarcane Bagasse for the Removal of Lead from Contaminated Water. *PeerJ* **2018**, *2018*, e5672. [CrossRef] [PubMed]

32. Samar, M.; Saxena, S. Study of Chemical & Physical of Perlite & Its Application in India. *Int. J. Sci. Manag.* **2016**, *5*, 70–80.

33. Engstrom, D.R. Long-Term Changes in Iron and Phosphorus Sedimentation in Vadnais Lake, Minnesota, Resulting from Ferric Chloride Addition and Hypolimnetic Aeration. *Lake Reserv. Manag.* **2005**, *21*, 95–105. [CrossRef]

34. Funes, A.; del Arco, A.; Álvarez-Manzaneda, I.; de Vicente, J.; de Vicente, I. A Microcosm Experiment to Determine the Consequences of Magnetic Microparticles Application on Water Quality and Sediment Phosphorus Pools. *Sci. Total Environ.* **2017**, *579*, 245–253. [CrossRef] [PubMed]

35. del Arco, A.; Álvarez-Manzaneda, I.; Funes, A.; Pérez-Martínez, C.; de Vicente, I. Assessing the Toxic Effects of Magnetic Particles Used for Lake Restoration on Phytoplankton: A Community-Based Approach. *Ecotoxicol. Environ. Saf.* **2021**, *207*, 111288. [CrossRef] [PubMed]

36. Gan, F.; Zhou, J.; Wang, H.; Du, C.; Chen, X. Removal of Phosphate from Aqueous Solution by Thermally Treated Natural Palygorskite. *Water Res.* **2009**, *43*, 2907–2915. [CrossRef]

37. Yin, H.; Yan, X.; Gu, X. Evaluation of Thermally-Modified Calcium-Rich Attapulgite as a Low-Cost Substrate for Rapid Phosphorus Removal in Constructed Wetlands. *Water Res.* **2017**, *115*, 329–338. [CrossRef]

38. De Andrade, J.R.; Oliveira, M.F.; Da Silva, M.G.C.; Vieira, M.G.A. Adsorption of Pharmaceuticals from Water and Wastewater Using Nonconventional Low-Cost Materials: A Review. *Ind. Eng. Chem. Res.* **2018**, *57*, 3103–3127. [CrossRef]

39. Liu, Y.; Tai, K.; Dillon, S.J. Growth Kinetics and Morphological Evolution of ZnO Precipitated from Solution. *Chemiistru Mater.* **2013**, *25*, 2927–2933. [CrossRef]

40. Pandey, S. A Comprehensive Review on Recent Developments in Bentonite-Based Materials Used as Adsorbents for Wastewater Treatment. *J. Mol. Liq.* **2017**, *241*, 1091–1113. [CrossRef]

41. Ho, Y.S.; McKay, G. Pseudo-Second Order Model for Sorption Processes. *Process Biochem.* **1999**, *34*, 451–465. [CrossRef]

42. Gandi, G.K.; Silva, V.M.T.M.; Rodrigues, A.E. Acetaldehyde Dimethylacetal Synthesis with Smopex 101 Fibres as Catalyst/Adsorbent. *Chem. Eng. Sci.* **2007**, *62*, 907–918. [CrossRef]

43. Anastopoulos, I.; Mittal, A.; Usman, M.; Mittal, J.; Yu, G.; Núñez-delgado, A.; Kornaros, M. A Review on Halloysite-Based Adsorbents to Remove Pollutants in Water and Wastewater. *J. Mol. Liq.* **2018**, *269*, 855–868. [CrossRef]

44. Biliani, S.E.; Vakros, J.; Manariotis, I.D. Screening of Raw and Modified Biochars from Food Processing Wastes for the Removal of Phosphates, Nitrates, and Ammonia from Water. *Sustainability* **2022**, *14*, 16483. [CrossRef]

45. Dada, A. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn 2+ Unto Phosphoric Acid Modified Rice Husk. *IOSR J. Appl. Chem.* **2012**, *3*, 38–45. [CrossRef]

46. Foo, K.Y.; Hameed, B.H. Insights into the Modeling of Adsorption Isotherm Systems. *Chem. Eng. J.* **2010**, *156*, 2–10. [CrossRef]

47. Edet, U.A.; Ifelebuegu, A.O. Kinetics, Isotherms, and Thermodynamic Modeling of the Adsorption of Phosphates from Model Wastewater Using Recycled Brick Waste. *Processes* **2020**, *8*, 665. [CrossRef]

48. *Method 4500-P E*; Phosphorus (Orthophosphate) by Ascorbic Acid Method. Standard Methods for the Examination of Water and Wastewater. APHA, APHAAWWA, WEF; American Public Health Association: Washington, DC, USA, 2017; pp. 4.146–4.148.

49. APHA; WEF; AWWA. *Standard Methods for the Examination of Water and Wastewater*, 20th ed.; Clesceri, L.S., Greenberg, A.E., Eaton, A.D.A., Eds.; American Public Health Association, American Water Works Association, Water Environment Federation: Washington, DC, USA, 2012.

50. Pai, S.C.; Tsau, Y.J.; Yang, T.I. PH and Buffering Capacity Problems Involved in the Determination of Ammonia in Saline Water Using the Indophenol Blue Spectrophotometric Method. *Anal. Chim. Acta* **2001**, *434*, 209–216. [CrossRef]

51. Fan, T.; Wang, M.; Wang, X.; Chen, Y.; Wang, S.; Zhan, H.; Chen, X.; Lu, A.; Zha, S. Experimental Study of the Adsorption of Nitrogen and Phosphorus by Natural Clay Minerals. *Adsorpt. Sci. Technol.* **2021**, *2021*, 4158151. [CrossRef]

52. Song, P.N.; Mahy, J.G.; Farcy, A.; Calberg, C.; Fagel, N.; Lambert, S.D. Development of novel composite materials based on kaolinitic clay modified with ZnO for the elimination of azo dyes by adsorption in water. *Results Surf. Interfaces* **2024**, *16*, 100255. [CrossRef]

53. Han, B.; Weatherley, A.J.; Mumford, K.; Bolan, N.; He, J.Z.; Stevens, G.W.; Chen, D. Modification of Naturally Abundant Resources for Remediation of Potentially Toxic Elements: A Review. *J. Hazard. Mater.* **2022**, *421*, 126755. [CrossRef] [PubMed]

54. Zacharias, I.; Biliani, I. Cultural Eutrophication Treatment with Innovative Clay-Based Materials. In Proceedings of the 3rd International Conference of Ecological and Environmental Engineering (3rd COEE), Poznań, Poland, 28 June 6–1 July 2022.

55. Abukhadra, M.R.; Abukhadra, M.R.; Ali, S.M.; Ali, S.M.; Nasr, E.A.; Nasr, E.A.; Mahmoud, H.A.A.; Mahmoud, H.A.A.; Awwad, E.M. Effective Sequestration of Phosphate and Ammonium Ions by the Bentonite/Zeolite Na-P Composite as a Simple Technique to Control the Eutrophication Phenomenon: Realistic Studies. *ACS Omega* **2020**, *5*, 14656–14668. [CrossRef] [PubMed]

56. Xiong, W.; Tong, J.; Yang, Z.; Zeng, G.; Zhou, Y.; Wang, D.; Song, P.; Xu, R.; Zhang, C.; Cheng, M. Adsorption of Phosphate from Aqueous Solution Using Iron-Zirconium Modified Activated Carbon Nanofiber: Performance and Mechanism. *J. Colloid Interface Sci.* **2017**, *493*, 17–23. [CrossRef] [PubMed]

57. Liu, Y.; Yan, C.; Zhao, J.; Zhang, Z.; Wang, H.; Zhou, S.; Wu, L. Synthesis of Zeolite P1 from Fly Ash under Solvent-Free Conditions for Ammonium Removal from Water. *J. Clean. Prod.* **2018**, *202*, 11–22. [CrossRef]

58. Alimohammadi, M.; Ayati, B. Remarkable Phosphate Removal from Saline Solution by Using a Novel Trimetallic Oxide Nanocomposite. *Water Reuse* **2021**, *11*, 410–424. [CrossRef]

59. Xu, Q.; Li, W.; Ma, L.; Cao, D.; Owens, G.; Chen, Z. Simultaneous Removal of Ammonia and Phosphate Using Green Synthesized Iron Oxide Nanoparticles Dispersed onto Zeolite. *Sci. Total Environ.* **2020**, *703*, 135002. [CrossRef]

60. Zamparas, M.; Drosos, M.; Georgiou, Y.; Deligiannakis, Y.; Zacharias, I. A Novel Bentonite-Humic Acid Composite Material Bephos[TM] for Removal of Phosphate and Ammonium from Eutrophic Waters. *Chem. Eng. J.* **2013**, *225*, 43–51. [CrossRef]

61. Kalla, N.; Khan, S. Effect of Nitrogen, Phosphorus Concentration, PH and Salinity Ranges on Growth, Biomass and Lipid Accumolation of Chlorella Vulgaris. *Int. J. Pharm. Sci. Res.* **2016**, *7*, 397–405. [CrossRef]

62. Zhi, Y.; Zhang, C.; Hjorth, R.; Baun, A.; Duckworth, O.W.; Call, D.F.; Knappe, D.R.U.; Jones, J.L.; Grieger, K. Emerging Lanthanum (III)-Containing Materials for Phosphate Removal from Water: A Review towards Future Developments. *Environ. Int.* **2020**, *145*, 106115. [CrossRef]

63. Shaheen, U.; Ye, Z.L.; Abass, O.K.; Zamel, D.; Rehman, A.; Zhao, P.; Huang, F. Evaluation of Potential Adsorbents for Simultaneous Adsorption of Phosphate and Ammonium at Low Concentrations. *Microporous Mesoporous Mater.* **2024**, *379*, 113301. [CrossRef]

64. Koh, K.Y.; Yang, Y.; Chen, J.P. Critical Review on Lanthanum-Based Materials Used for Water Purification through Adsorption of Inorganic Contaminants. *Crit. Rev. Environ. Sci. Technol.* **2022**, *52*, 1773–1823. [CrossRef]

65. Omorogie, M.O.; Agunbiade, F.O.; Alfred, M.O.; Olaniyi, O.T.; Adewumi, T.A.; Bayode, A.A.; Ofomaja, A.E.; Naidoo, E.B.; Okoli, C.P.; Adebayo, T.A.; et al. The Sequestral Capture of Fluoride, Nitrate and Phosphate by Metal-Doped and Surfactant-Modified Hybrid Clay Materials. *Chem. Pap.* **2018**, *72*, 409–417. [CrossRef]

66. Zamparas, M.; Zacharias, I. Restoration of Eutrophic Freshwater by Managing Internal Nutrient Loads. A Review. *Sci. Total Environ.* **2014**, *496*, 551–562. [CrossRef] [PubMed]