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Adsorption of Nitrate Ions Using Magnesium-Loaded Bamboo Powder and Nano-Sized Crushed Oyster Shells

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Abstract: Excess nitrate ions should be avoided in agriculture as they are absorbed by plants and ingested by humans, which can have serious effects on soil and groundwater. In this study, environmentally friendly bamboo flour and nano-sized oyster shells were used as adsorbents. The equilibrium time for nitrate adsorption was found to be short, less than five minutes, and the treatment temperature had little effect on adsorption. The adsorption capacity and adsorption mechanism were investigated using experiments and adsorption isotherms. Bamboo powder treated with magnesium chloride (Mg bamboo), crushed oyster shell (oyster shell), and hydrogel induced with sodium alginate (hydrogel) were used. The maximum adsorption of nitrate ions on the magnesium-treated bamboo flour was estimated to be 399 mg NO_3^-/g by the Dubin–Radushakevich equation (correlation coefficient 0.84), with the Langmuir (correlation coefficient 0.91) and Freundlich (correlation coefficient 0.91) equations also fitting relatively well. The D-R equation (correlation coefficient 0.938) and Freundlich equation (correlation coefficient 0.943) also fitted oyster shells relatively well. The maximum adsorption was estimated at 354 mg NO_3^-/g. In oyster shell treatments where phosphate and nitrate ions were present, it was observed that both substances were adsorbed simultaneously. For the hydrogels, only the D-R equation (correlation coefficient 0.944) and the Freundlich isotherm were applicable. The maximum adsorption was estimated at 156 mg/g.

Keywords: nitrate adsorption; bamboo powder; nano-sized oyster shells; isotherm equations

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1. Introduction

The use of abandoned bamboo forests as a resource, which is a social problem in Japan and Southeast Asia, is also being promoted. Oyster shells from the fishing industry are also being considered for use in various fields, as they contain calcium as a major component. The premise of this paper is to apply these by-products, bamboo flour and oyster shells, to agricultural soils to prevent excess nitrate ions from being adsorbed by plants or leaking into environmental water, or to pre-adsorb nitrogen and use it as a nitrogen material, supplying an environmentally friendly alternative to chemical fertilizers. For this purpose, the adsorption capacity was determined using a batch method to determine the suitability of the Langmuir, Freundlich, and Dubin–Radushakevich (D-R) equation; commercial bamboo flour that passed the 178 μm sieve was treated with magnesium chloride to increase the adsorption capacity. Commercial oyster shell powder that passed the 50% cumulative particle size (420 nm) was fixed to the hydrogel to check the adsorption capacity, ensure separation, and measure changes in the capacity.

In existing reports, plant biomass is soaked in a magnesium chloride solution and carbonized at high temperatures. The immobilized magnesium oxide is said to have a positive or negative charge depending on the pH, and electrostatically binds to hydrogen in nitric and phosphoric acids [1]. Calcium oxide is expected to adsorb phosphoric acid through the electrostatic effect with intramolecular oxygen [2]. It is also thought to be able to adsorb nitric acid although there are differences between magnesium and nitric acid. In the present study, the experiments were conducted without calcination operations. This is because the oyster shell fine powder is produced by grinding under heat and pressure.

Most of the nitrate ions consumed by humans come from vegetables. Although nitrate ions are not directly harmful to the human body, they are completely unnecessary for humans, and it has been suggested that their depletion may have adverse effects.

The accumulation of nitrate ions in vegetables is also considered to be an important factor in environmental impacts such as groundwater pollution due to the excessive use of nitrogen fertilizers [1–6]. From this perspective, this paper presents an environmentally friendly method of waste recycling.

The use of bamboo powder and oyster shells as adsorbents for nitrate ions is desirable from both safety and environmental impact perspectives.

In this study, (1) bamboo powder loaded with magnesium chloride and (2) oyster shell powder with a D50 diameter of 420 nm were used to improve the adsorption capacity of nitrate ions. It was reported that the application of bamboo powder reduced nitrate ions in the soil solution [7]. Bamboo powder, as the name suggests, is produced by grinding cultivated bamboo in a grinder. In modern times, it is mainly used in the agricultural and domestic sectors to deodorize and compost food waste.

There are four main uses.

(1) It can be used as a soil conditioner in horticulture. It improves the soil itself (water retention, heat retention, aeration, etc.) and the microbiological properties of the soil in rice paddies and fields, creating an environment suitable for plant growth [8,9]. The [lactic acid bacteria + porosity] of bamboo flour acts on soil microorganisms [10].
(2) It can be used as a raw material for animal feed (cattle, pigs, chickens). The feed is prepared by mixing bamboo flour with molasses and lactic acid bacteria, stirring well and compressing. This is rolled and wrapped in foil and fermented for 40 days [11–13].
(3) It can be used for deodorizing animal excrement and promoting compost fermentation. Ordinary bamboo powder can be spread on the floor of livestock sheds to reduce the odor of the sheds. The porous structure of bamboo powder absorbs bad odors [14].
(4) The porous nature of bamboo powder makes it capable of absorbing heavy metals, phosphorus, and other constituents [15,16].

Oyster shell powder can be used as a concrete material to replace river sand [17,18]. As an adsorbent, it is immobilized as a composite material and has been reported to remove heavy metals and fluorine [19,20].

Bamboo charcoal is also used to remove phosphate and nitrate ions [21–29]. In this study, we wanted to increase the nitrate ion adsorption capacity while leaving the bamboo powder intact in order to maintain its function as a habitat for lactic acid bacteria, so we decided to treat the bamboo powder with magnesium chloride, referring to a report on the magnesium chloride treatment of bamboo charcoal [24].

Not carbonizing the bamboo powder can also contribute to cost reduction.

The effective use of eggshells, which are mainly composed of 97% calcium carbonate, for nitrate ion adsorption has been studied, and 70% adsorption has been reported at an initial concentration of 100 ppm [22]. The reduction of nitrate ions by nano-sized zero-valent iron, and its use as a composite material of eggshells, supported by zero-valent iron, have also been studied [23]. Based on the above, it was speculated that nano-sized calcium (oyster shell-based) would be effective. It was first tested in suspension, and then fixed in sodium alginate as a hydrogel.

The aim of this study was to utilize these bamboo and oyster powders for the adsorption of nitrate ions, thereby contributing to the utilization of secondary materials and improving the soil environment. To this end, a low-cost method to increase the separation capacity of nitrate ions was proposed.

2. Materials and Methods

2.1. Bamboo Powder and Oyster Shells

The bamboo powder and oyster shells used in this study were both commercially available products. In total, 200 g of domestic bamboo powder, passed through a 178-micron sieve, was purchased from Nakawood Co., (Tokushima, Japan) Ltd. via Amazon (Tokyo, Japan). EDS component analysis was performed using JEOL JSM-7001F (JEOL Ltd., Tokyo, Japan).

Figure 1 shows an optical micrograph of the bamboo powder (OLYMPUS CX23). The particle size distribution was measured by laser diffraction using Horiba Partica LA-960V2 (Kyoto, Japan). The results showed that 50% of the mass fraction in transit was 15.1 μm.

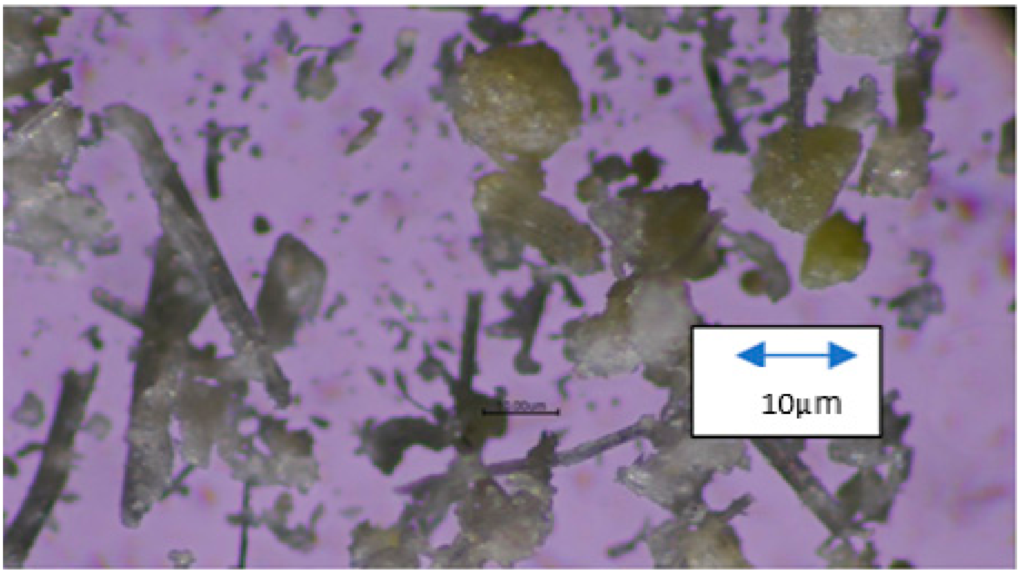


Figure 1. Optical micrograph of the bamboo powder.

Table 1 provides published data on the particle size relationship for nano-sized oyster shells. The 50% cumulative particle size is 420 nm.

Table 1. Published particle size distributions of nano-sized. oyster shell powders (copyright© 2011 KURE KOU IKI SHOUKOUKAI SEINENBU).

	Nano-Powder Oyster Shell
Median diameter [μm]	8.42
Mode diameter [μm]	9.55
Arithmetic mean [μm]	8.89
Geometric mean [μm]	4.03
50% cumulative [μm]	0.42 μm (420 nm)

Oyster shells containing nano-sized calcium were purchased from Kure Brand Corporation (Kure, Hiroshima, Japan). The nano-sized oyster shell powder was developed as a project of the regional chamber of commerce and industry of Kure City, Hiroshima Prefecture, with the aim of developing and marketing a new product using oyster shells, which are discarded as a by-product resource. It is characterized by calcined oyster shells with an average particle size at the nano-level. The manufacturing process involves pressing oyster shells at around 300 °C using a patented process (an instantaneous high-temperature, high-pressure sintering method), which maintains a weak alkalinity of pH (9.1) and is expected to have antibacterial and deodorizing effects, because it is not subjected to high-temperature sintering. All reagents used in this research were special-grade products of Kanto Chemical. Figure 2 shows the elements detected by the EDS analysis of oyster shells and bamboo powder. Judging from the ratio of the number of calcium, carbon, and oxygen atoms in the oyster shells, it is believed that there is a lot of calcium carbonate. Magnesium and chlorine were also detected. Bamboo powder contains a lot of carbon and oxygen. Since Mg makes up 0.42%, magnesium oxide is also present, and in this study, magnesium chloride was added to forcibly increase the proportion of Mg.

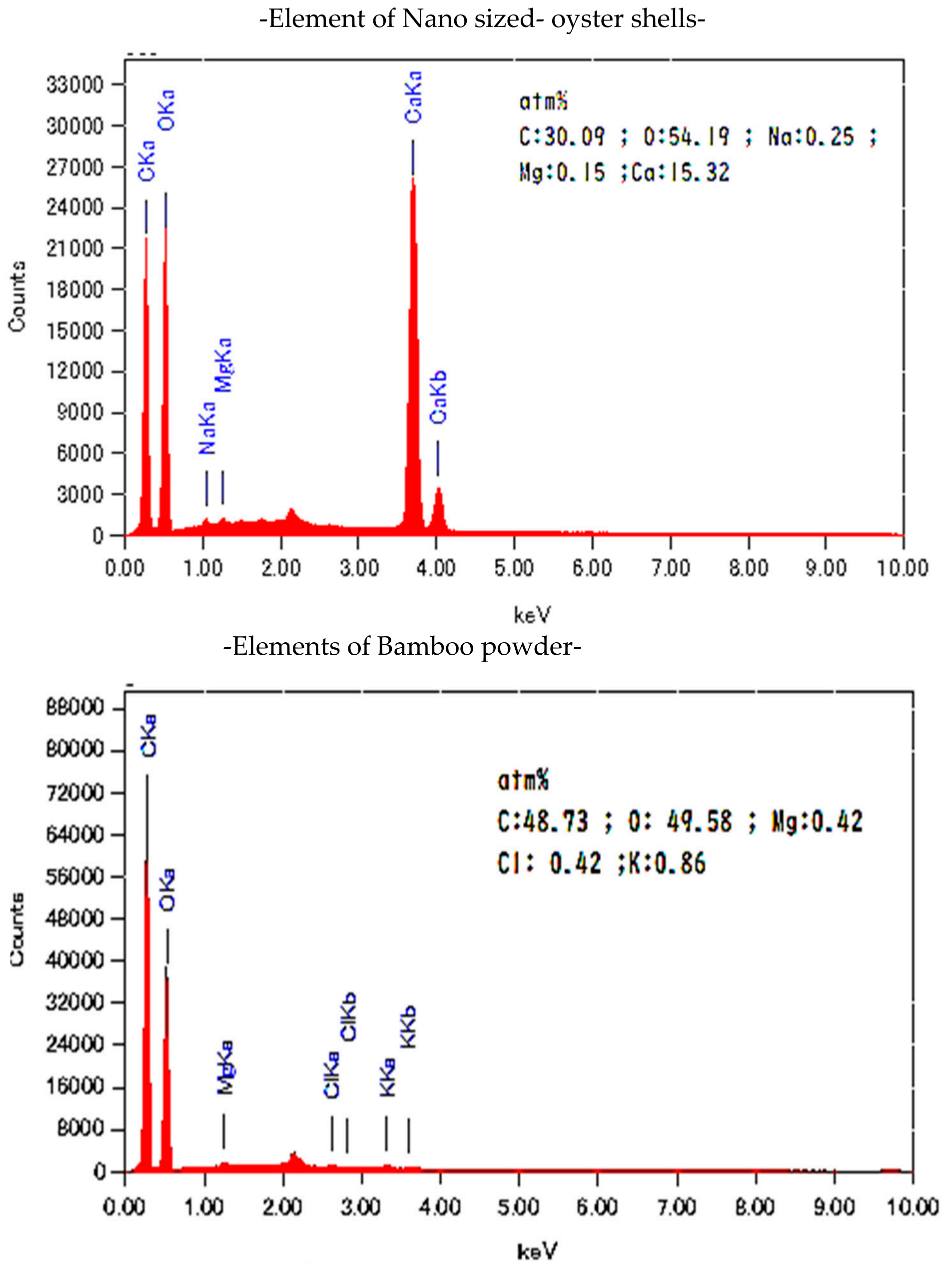


Figure 2. EDS element analysis of oyster shell powder and bamboo powder.

2.2. Analysis of Nitrate and Phosphate Ions

For nitrate ions, the following official methods are used: 4500-NO_3^- Nitrate ions (NITRATE). The content of this section is based on the latest edition of the Standard Method for the Examination of Water and Wastewater, 24th edition. Phosphate ions have been analyzed using 4500-P phosphorus. Mg was also analyzed using the standard colorimetric method.

Figure 3 shows the calibration curves for nitrate, phosphate, and magnesium ions used to determine the concentrations. Commercially available 1000 mg/L standards were used and diluted to the appropriate concentrations. All calibration curves have correlation coefficients of 0.983 or greater and are of practical use. The calibration curves did not pass through the origin without considering the intercept value, which was 0.017, 0.27, and 0.23 mg/L for nitrate, phosphate, and magnesium ions, respectively, which are the detection limits. The experiment was examined in the range of the calibration curves above the detection limit.

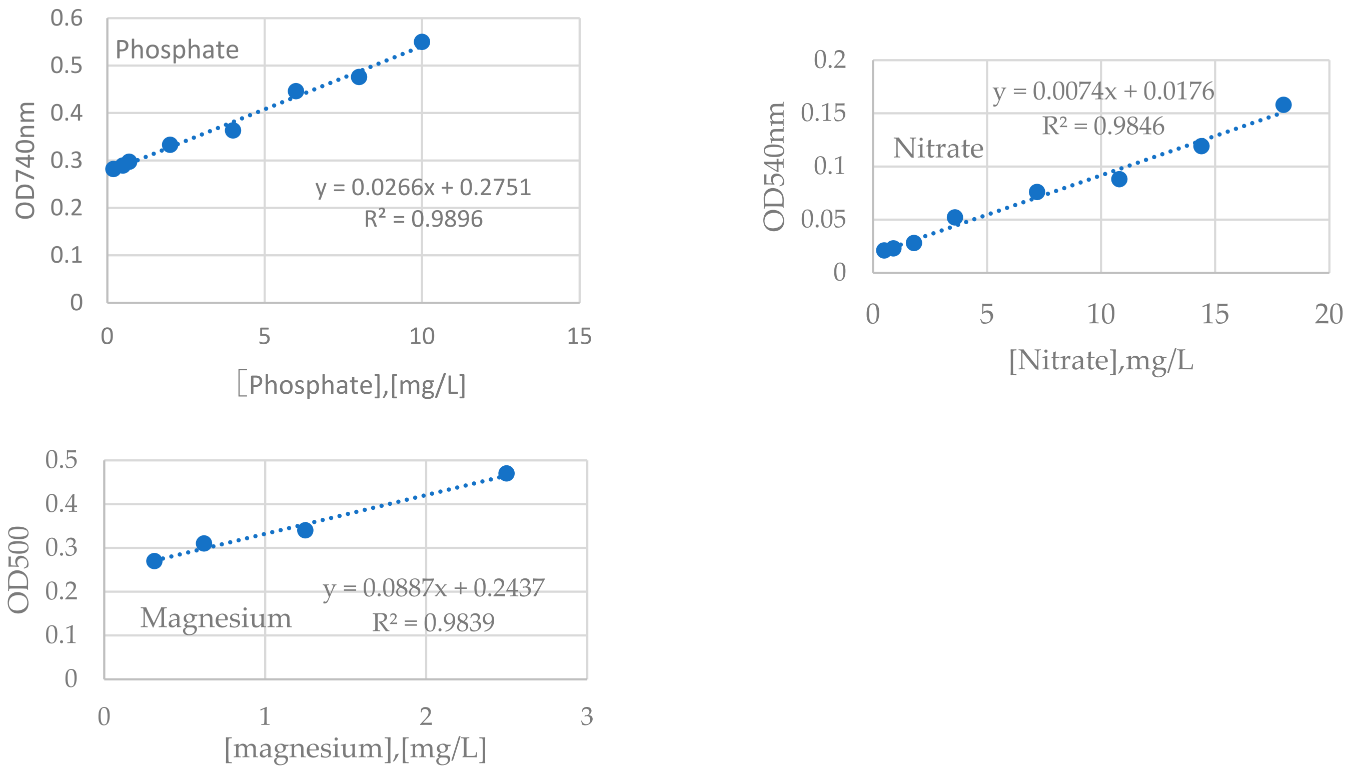
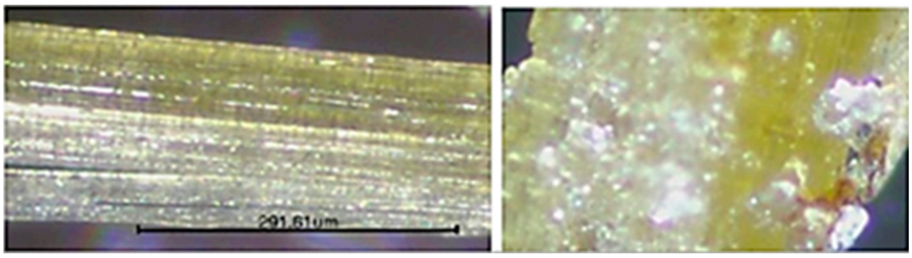


Figure 3. Calibration curve. Each of these was used with a standard solution of 1000 mg/L diluted to the respective concentration.

2.3. Magnesium Chloride Treatment of Bamboo Powder

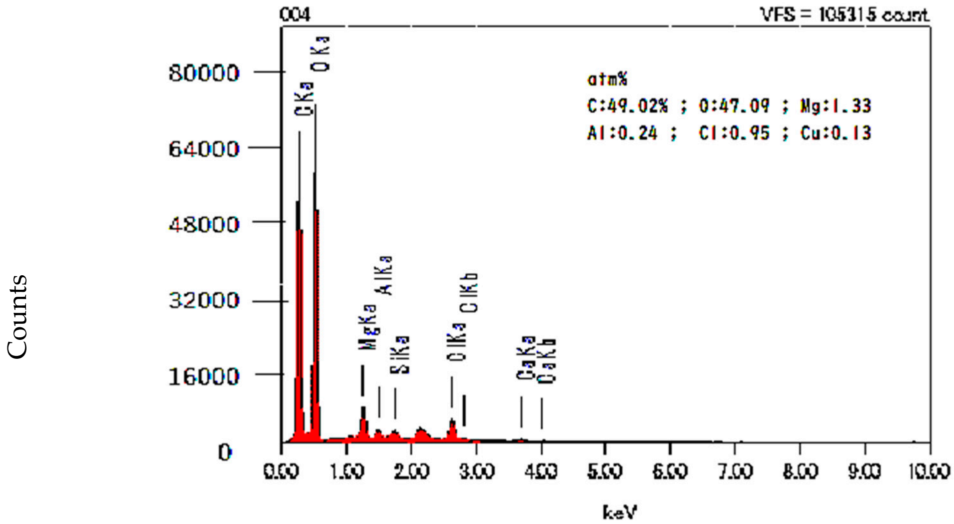
The treatment procedure is as follows:

① Put 101.65 g of magnesium chloride hexahydrate into a 1 L beaker, add 1 L of distilled water, and mix well.② Put 50 g of bamboo powder into a 1 L beaker, add 900 mL of the prepared magnesium chloride aqueous solution, and stir for 24 h at 60 °C with a heater.③ After stirring for 24 h, filter the solution obtained in into a 200 mL beaker and measure the Mg concentration in the filtrate. Figure 4 shows the changes in the bamboo powder surface before and after the magnesium chloride treatment. The results of the EDS analysis are also shown. Mg increased to 1.33%, and chlorine also increased to 0.95%.



Bamboo powder. Magnesium on bamboo powder.

(**a**)



(**b**)

Figure 4. Changes in the shape and elements of the bamboo powder as a result of magnesium loading. Electron microscopy and EDS component analysis were performed by JEOL Corporation using the JSM-7001F optical microscope OLMPUS CX23. (**a**) Changes in bamboo powder shape due to magnesium treatment. (**b**) EDS elements analyzed of Mg-Bamboo powder.

2.4. Nano-Size Oyster Shell Powder Hydrogel

In total, 200 mL of 3% nano-calcium was added to 200 mL of 4% sodium alginate solution and stirred at 500 rpm using a magnetic stirrer to prevent precipitation. Meanwhile, a microtube pump (Tokyo Rika MP-100, Eyela Tokyo Rikakikai. Co., Ltd., Tokyo, Japan) was used to pump this solution with 3% calcium chloride solution at a flow rate of 1 mL/min to obtain beads. The beads were washed with tap water and then used in the experiment. Solutions of 1000 mg/L each of nitrate and phosphate were prepared, and the adsorption process was carried out at different mixing ratios to investigate changes in concentration.

2.5. Adsorption Experiments

Treated bamboo powder or nano-calcium was placed in a 6-well cell plate, and 10 mL of each solution was added under different conditions. A Waken Kogyo temperature-controlled multi-shaker incubator was used and stirred at 25 °C and 120 rpm. The treated solution was collected with a syringe, and a holder with a 0.45 µm mem-brane filter was attached to the end. The filtrate was analyzed for nitrate or phosphate ions by absorption spectroscopy. The decrease in concentration on the liquid side is assumed to be due to adsorption, but to confirm this, the balance of components eluted from the bamboo powder and the nano-sized adsorbent was measured using a soil analyzer [AIR WATER BIODESIGN Corporation]. This is based on the principle of the simultaneous colorimetric determination of soil nutrients (nitrogen, phosphorus, potassium, calcium, and magnesium) using a coloring reagent and a cartridge.

2.6. Experimental Procedure Plan

In each of the following experiments, the weight of the adsorbent, the volume of the treatment solution, the pH the nitrate concentration before and after the treatment were measured.

(i) The effect of mixing time was studied. The adsorbent and solution placed on each perforated plate, and each sample was quickly collected and filtered through a 0.4 µm membrane filter for analysis. The initial nitrate ion concentration was set at approximately 800 mg/L, and the nitrate nitrogen value was 200 mg/L. The pH was measured using a pH electrode (LAQUAtwin Horiba, Kyoto, Japan).

(ii) The effect of temperature was studied. In Section 2.5, the temperature of the multi-shaker incubator was set at to 25 °C, but in the experiments, it was also changed to 35 °C and 45 °C, respectively.

(iii) Adsorption isotherms were kept at a constant temperature and solid/liquid ratio and at different initial concentrations. The initial concentration was 0.05 M nitric acid standard solution. To study the effect of pH, a few drops of 1M NaOH or 1M H2SO4 were added.

Table 2 shows the orthogonal experimental design. Detailed experimental conditions are displayed. The main issues discussed are temperature, adsorption capacity and the effect on the coexisting substances.

Table 2. Orthogonal test factors and leve-ls.

Level					
Mg-Bamboo	Temeprature, pH	Volume [mL]	Tim [min]	adsorbent [g]	Initial Concentration [mg/L]
1	25 °C	4	0~40	0.08	800
2	35 °C	4	0~40	0.08	800
3	45 °C	4	0~40	0.08	800
Oyster shell	Temeprature, pH	Volume [mL]	Tim [min]	adsorbent [g]	Initial Concentration [mg/L]
1	25 °C	4	0~40	0.08	800
2	35 °C	4	0~40	0.08	800
3	45 °C	4	0~40	0.08	800
Hydro gel	Temeprature, pH	Volume [mL]	Tim [min]	adsorbent [g]	Initial Concentration [mg/L]
1	25 °C	4	0~40	0.1	800
2	35 °C	4	0~40	0.1	800
3	45 °C	4	0~40	0.1	800
Level					
Mg-Bamboo	Adsorption Capacity [mg/g]	Volume [mL]	Tim [min]	adsorbent [g]	Initial Concentration [mM]
1	25 °C	8	0~120	0.03	50 mM, 40 mM, 30 mM, 25 mM, 20 mM, 10 mM
2	26 °C	9	0~120	0.03	5 mM, 4 mM, 3 mM, 2.5 mM, 2 mM, 1 mM
Oyster shell	Adsorption Capacity [mg/g]	Volume [mL]	Tim [min]	adsorbent [g]	Initial Concentration [mM]
1	25 °C	8	0~120	0.03	50 mM, 40 mM, 30 mM, 25 mM, 20 mM, 10 mM
2	25 °C	8	0~120	0.03	5 mM, 4 mM, 3 mM, 2.5 mM, 2 mM, 1 mM
Hydro gel	Co-Exsiting (N-P mixture)	Volume [mL]	Tim [min]	adsorbent [g]	Initial Concentration [mM]
1	25 °C	8	0~120	0.11	Phosphate 1000 mg/L and Nitrate 1000 mg/L
2	25 °C	8	0~120	0.11	P/(N + P) 0, 0.1, 0.2, 0.3, 0.4, 0,5
3	25 °C	8	0~120	0.11	P/(N + P) 0.6, 0.7, 0.8, 0.9, 1.0

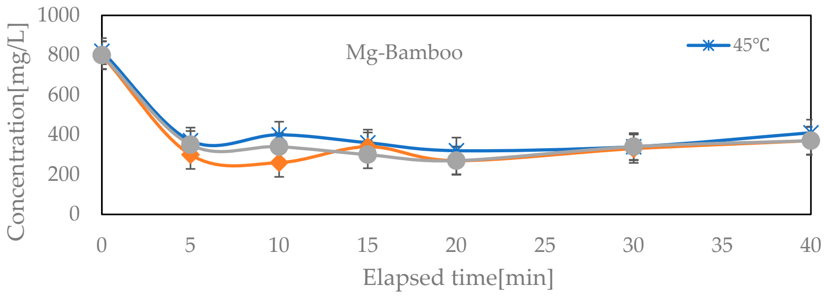
3. Results and Discussion

3.1. Nitrate Removal Using Mg-Treated Bamboo Powder and Bamboo Charcoal

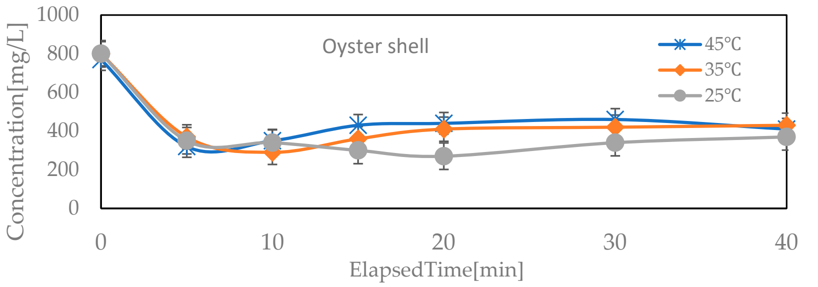
Magnesium was measured by atomic absorption spectrophotometry [Shimadzu AA-5800]. The results showed that the loading was 101 mg/g.

3.2. Effect of Temperature

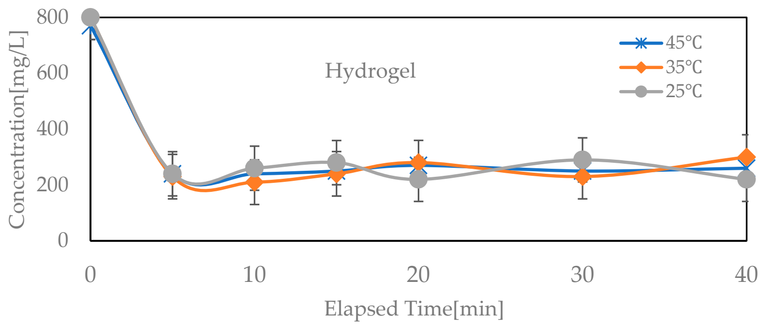
The results of changing the temperature for the Mg bamboo, oyster shell, and gel are shown in Figure 5. In conclusion, for all temperatures and adsorbents, the concentration was reduced to half in 5 min, after which it could be considered to plateau, although there was some fluctuation. In this experiment, the concentration decreased over time and no equilibrium was reached, so it was not possible to obtain the reaction constant as a pseudo-first-order or pseudo-second-order reaction. However, the results up to 10 min showed that the temperatures were 45 °C, 25 °C, and 35 °C in order of increasing concentration, although there were fluctuations due to re-elution, and 35 °C was estimated to be the optimum temperature. After that, however, there were some fluctuations that could be due to re-elution. The equilibrium pH decreased sequentially with increasing temperature in (i) Mg bamboo, reaching 3.6 at 45 °C. Oyster shell (ii) showed little change, ranging from 8.4 to 8.9. (iii) Hydrogels ranged from 7.7 to 8.1.



Adsorption dose: V = 4 mL, m = 0.08 g of Mg bamboo (pHe: 3.5–6.9), initial concentration (800 ppm in each case), and at 25, 35, and 45 °C



Adsorption dose: V = 4 mL, W = 0.08 g of oyster shell (pHe: 8.4–8.9), initial concentration (800 ppm in each case), and at 25, 35, and 45 °C



Adsorption dose: V = 4 mL, W = 0.10 g of hydrogel (pHe: 7.7–8.1), initial concentration (800 ppm as nitrate ions), and at 25 °C, 35 °C, and 45 °C.

Figure 5. The effects of the temperature of adsorption on each adsorbent.

Figure 6 shows the possible post-equilibrium pH changes due to the addition of sulfuric acid. (i) For Mg bamboo, treatment on the acidic side is undesirable. The equilibrium pH of the oyster shell is high, with an optimum range around 9. Hydrogels are less affected by pH fluctuations and can be kept constant.

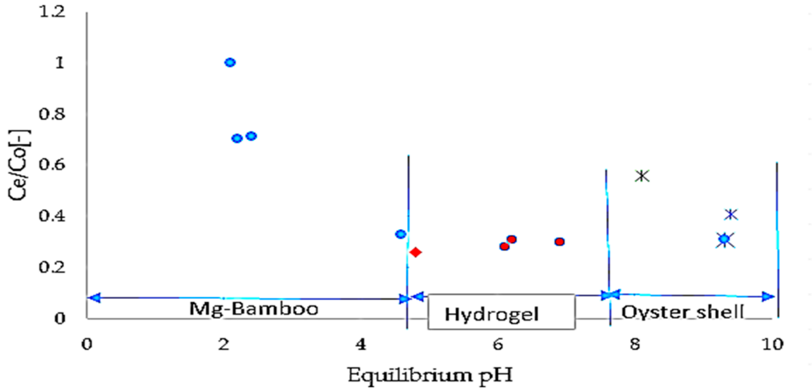


Figure 6. The effect of temperature on equilibrium pH.

Figure 7 shows the results of the elemental analysis of the nitrogen-adsorbed hydrogels by EDS analysis. Nitrogen accounted for 14.5% of the total. However, it could not be confirmed by EDS in Mg bamboo and oyster shell. On the other hand, the nitrogen detected in the hydrogels was not only fixed internally, but also originally contained calcium on the gel surface, suggesting that it was present as a more uniform adsorption on the surface.

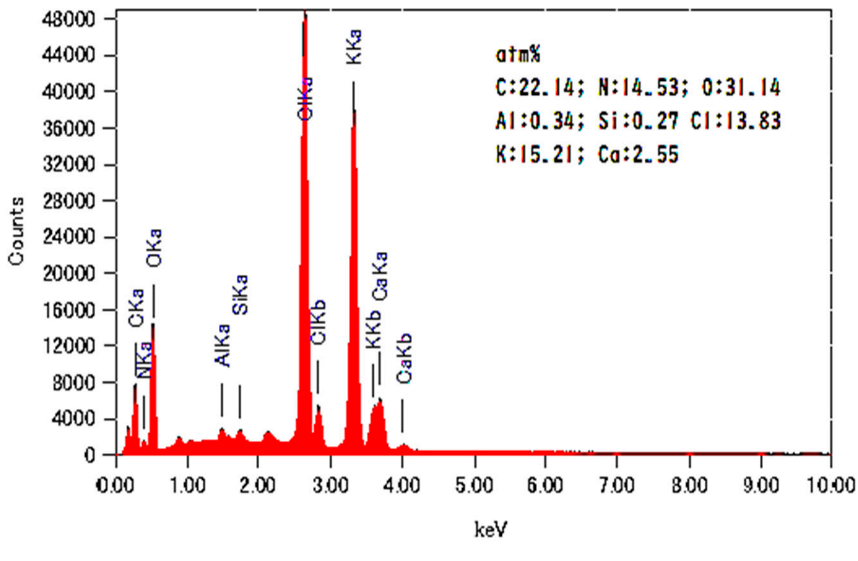
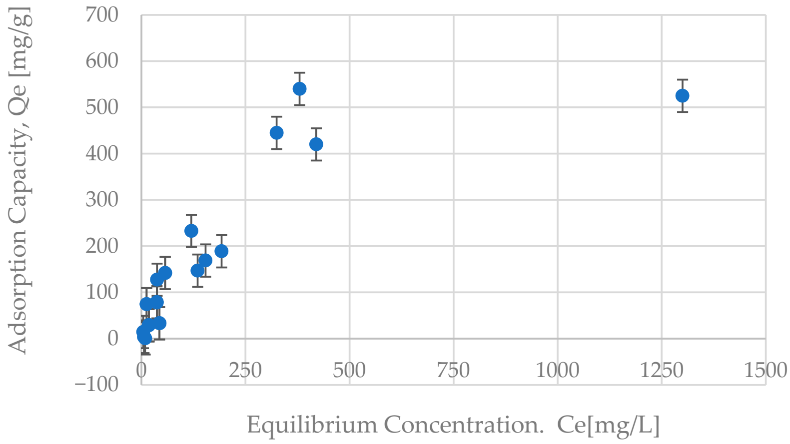


Figure 7. Changes in element hydrogel as a result of adsorption.

3.3. Nitrate Adsorption Mechanism

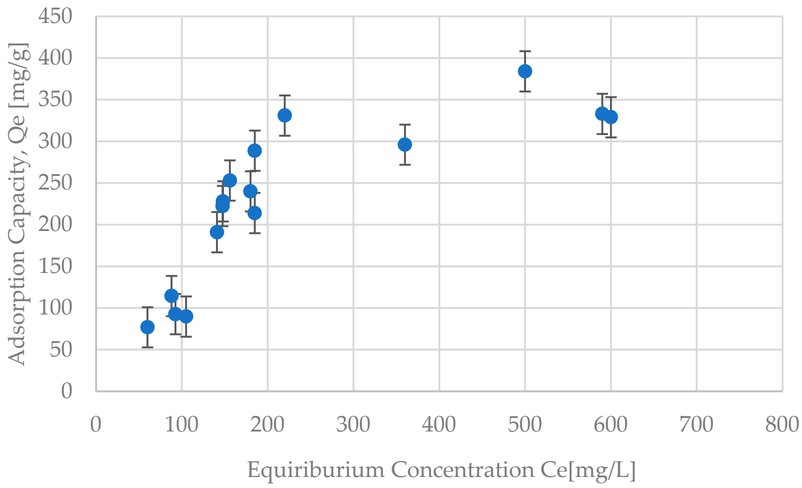
Reference has been made to treating bamboo charcoal with calcium chloride to remove phosphate ions [22]. As no heat is applied to the magnesium to oxide it, the chloride ions of the magnesium chloride are exchanged for monovalent nitrate ions. This is similar to reports of biochar treated with magnesium or calcium chloride, where nitrate ions are selectively treated [22].

Figures 8–10 show the isothermal adsorption curve of Mg bamboo, oyster shells, and hydrogel, respectively.



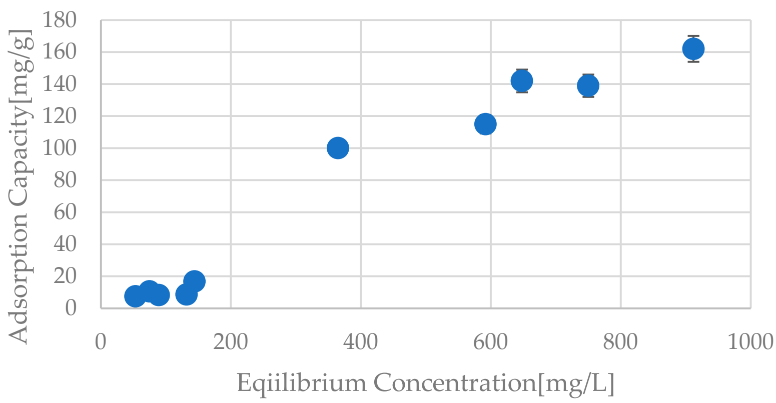
Adsorption dose: V = 8 mL, W = 0.03 g of H Mg bamboo, initial concentration. The initial concentration of the nitric acid standard solution was 0.05 M, which was then diluted stepwise for use in the experiment.

Figure 8. Adsorption isotherms of nitrate ions on magnesium-loaded bamboo powder (25 °C).



Adsorption dose: V = 8 mL, W = 0.03 g of oyster shell. The initial concentration of the nitric acid standard solution was 0.05 M, which was then diluted stepwise for use in the experiment.

Figure 9. Adsorption isotherms of nitrate ions on oyster shell (25 °C).



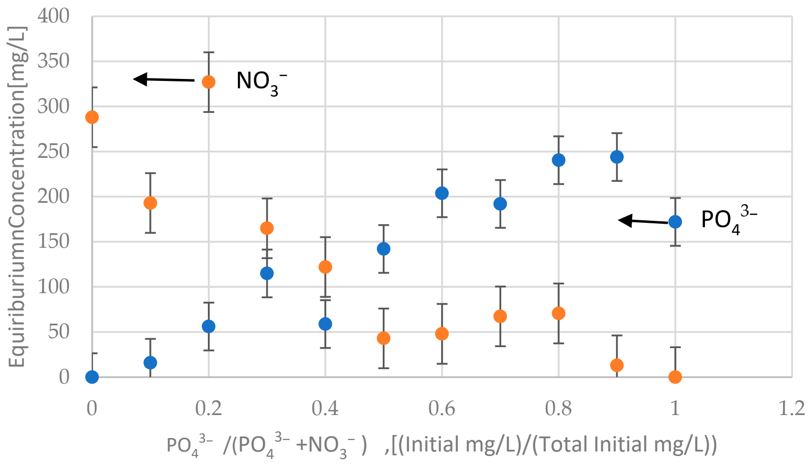
Adsorption dose: V = 8 mL, W = 0.03 g of oyster shell. The initial concentration of the nitric acid standard solution was 0.05 M, which was then diluted stepwise for use in the experiment.

Figure 10. Adsorption isotherms of nitrate ions on hydrogel (25 °C).

Yokoyama et al. dropped calcium chloride onto coffee charcoal to carbonize it and adsorb nitrate ions, and found that about 1 mmol/L of nitrate nitrogen was removed [23]. A composite material of bamboo charcoal and montmorillonite adsorbed 512 mg/g of nitrate ions [24]. This result for nitrate nitrogen was almost the same as that of Mg bamboo in this experiment. At a local sewage treatment plant, it was reported that nitrate was reduced by 400 mg/L by filling the denitrification tank with bamboo powder [25,26]. Bamboo powder-filled columns have been studied for the denitrification treatment of nitrate-contaminated groundwater [27]. The adsorption in this experiment can be considered similar to that of a biomass anion exchange resin.

3.4. Nitrate Removal in the Presence of Phosphoric Acid

The results are shown in Figure 11. The horizontal axis shows the ratio of phosphate ions to the total amount of phosphate + nitrate ions. The vertical axis shows the equilibrium concentration. For example, when the ratio is 0.2, the initial concentration of phosphoric acid is 200 mg/L, and that of nitric acid is 800 mg/L. The phosphate ion dropped to 52 mg/L from the equilibrium concentration, and the nitric acid to 338 mg/L. Both nitrate and phosphate ions were adsorbed at ratios of 0.2–0.8. The adsorption of both ions is considered an advantage, but the adsorption mechanism is not ion exchange and is, therefore, somewhat less selective.



Adsorption dose: V = 8 mL, W = 0.03 g of shell. The initial concentration of the nitric and phosphoric acid standard solution was 0.05 M, which was then diluted stepwise for use in the experiment at 25 °C.

Figure 11. Adsorption isotherms of nitrate ions on oyster shell (25 °C).

3.5. Analysis of the Adsorption Curve

Table 3 shows the results of applying Equations (1) through (3) for Figures 8–10. The adjustment equations include empirical equations (Temkin, P-R, and Toth models), monolayer chemisorption equations (Langmuir), multilayer physisorption equations (Freundlich and Arnanovich), and ion exchange models [30].

Table 3. The isotherm model parameters computed from intercept and slope of these coefficient parameters.

	Langmuir Equation			Freundlich Equation			D-R Equation		
	K_L	Q_m	R^2	n	k	R^2	K	Q_m	R^2
Mg bamboo	0.0047	625	0.916	1.42	5.71	0.911	0.0005	399	0.842
Oyster shell	0.0050	476	0.904	0.85	3.78	0.943	0.0016	354	0.938
Hydrogel	-	-	0.338	0.70	6.05	0.947	0.114	156	0.994

As the aim of this study is to adsorb excess nitrate in the soil after adsorption and subsequently maintain its function as a slow-release fertilizer as a nitrogen supply material, the application of the widely accepted Langmuir and Freundlich formulae is discussed.

The adsorption capacity Q_e [mg/g] was used for the evaluation. The calculation formula is Equation (1).

$$Q_e = \left[\frac{C_i - C_e}{W}\right] \times V \tag{1}$$

The initial concentration is C_i (mg/L), the equilibrium concentration is C_e (mg/L), the batch test capacity is V (L), and the adsorbent volume is W (g).

The adsorption mechanism is then divided into the Langmuir formula for monolayer molecular adsorption and the Freundlich formula for other mechanisms. The respective formulae are given in (2) and (3). The adsorption mechanism is then divided into the Langmuir formula for monolayer molecular adsorption and the Freundlich formula for other mechanisms.

1. Langmuir Equation:

$$\frac{C_e}{Qe} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \tag{2}$$

2. Frundlich Equation:

$$\log(Q_e) = \log K + \frac{1}{n}\log(C_e) \tag{3}$$

Q_m (mg/g): maximum adsorption capacity; K_L: constant; N, K: constant.

3. Dubin–Radushakevich (D-R) equation:

$$\ln(Q_e) = \ln(Q_m) - K\varepsilon^2 \tag{4}$$

$$\varepsilon = \mathrm{RTln}1 + 1/C_e$$

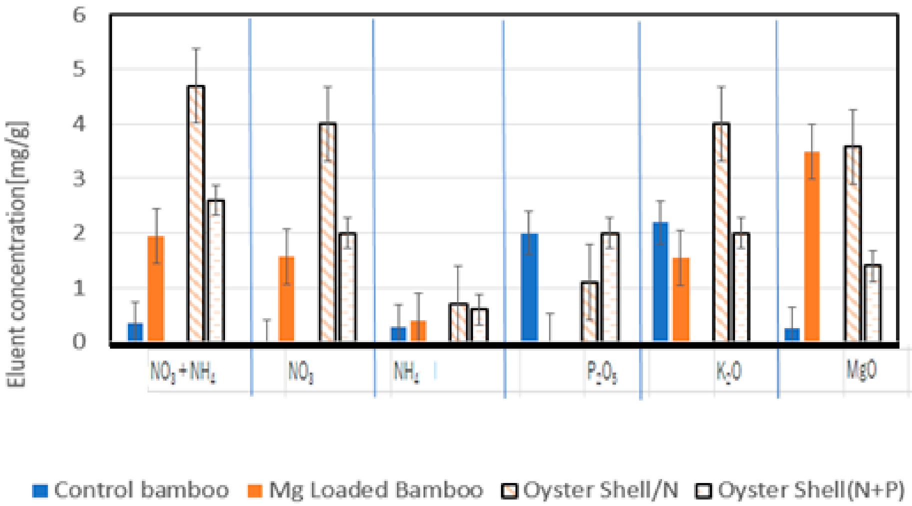
R = universal gas constant (8.314 J/K/mol); K = active coefficient; ε = Polanivi constant (kJ/mol).

Table 3 shows the parameters obtained.

① Comparing the correlation coefficients, there was no significant difference between the Langmuir and Freundlich equations for Mg bamboo, with a correlation coefficient of 0.91. On the other hand, the D-R equation was 0.84. The difference between the Langmuir and Freundlich equations is that the former is a single-layer chemical adsorption, while the latter is a multilayer physical adsorption. The D-R equation has a parameter related to the free energy in the coefficient. ② In the case of oyster shells, the particle size is small and uniform, so the correlation coefficients of both equations are high, and the Freundlich equation has a slightly better fit. The correlation coefficient of the D-R equation was almost the same as that of the Freundlich equation. ③ When hydrogel was applied, the Langmuir equation did not fit at all, and the Freundlich equation showed a correlation coefficient of over 0.94. The correlation coefficient of the D-R equation was 0.994, which is very linear.

It is clear from the photographic material in Figure 3 that Mg is not uniformly loaded on the bamboo flour, suggesting that both chemisorption and physisorption occur. This hypothesis is supported by the fact that the parameter n in the Freundlich equation is 1.4, which is greater than 1, indicating a higher retention rate. The correlation coefficient of the Freundlich isotherm for the oyster shell was 0.94. This is attributed to the finer and more uniform particles of the oyster shell compared to the bamboo flour. For the hydrogels, the Freundlich equation was regressed with a correlation coefficient of 0.94, but the Langmuir equation could not be correlated. This result may be due to the presence of calcium on the gel surface and the use of a 3% calcium chloride solution in the gel preparation process, which immobilized nitrogen. As a result, nitrogen was only detected in the hydrogels by EDS analysis. The presence of oyster shell in the hydrogel may also have influenced these results. The maximum adsorption calculated using the Langmuir equation was estimated to be higher than that in Figures 8–10. On the other hand, the estimates using the D-R method can be judged to be more reflective of the experimental results.

The following experiment will help to confirm the adsorption components of Mg bamboo and oyster shell. The presence of nitrogen was detected only in the hydrogel by the electron spin resonance (EDS) method. As a result, Mg bamboo and oyster shell powder, which were previously confirmed to reduce the solution concentration without affecting the solid matter, will be further verified by the extraction method. This method is commonly used in soil analysis to determine the availability of nitrogen and phosphorus. The soil analyzer automatically detects the six components using the absorption method. Figure 12 shows the results of the analysis of Mg bamboo using a soil analyzer for the solution extracted with citric acid as an available nitrogen extraction method after nitrogen adsorption, and the results of the analysis of oyster shells using a soil analyzer for nitrogen adsorption and simultaneous adsorption of phosphorus and nitrogen.



Adsorption dose: V = 8 mL, W = 0.03 g of **oyster shell/N**. The initial concentration of the nitric acid: 100 mg/L oyster shell (N + P). The initial concentrations (each 50 mg/L) and phosphoric acids standard solution were 0.05 M, which was then diluted stepwise for use in the experiment. Adsorption dose: V = 8 mL, W = 0.03 g of bamboo, Mg **bamboo, and oyster shell/N**. The initial concentration of the nitric acid (100 mg/L).

Figure 12. The results of the analysis of the extracted solution using a soil analyzer for the solution extracted with citric acid as an available nitrogen extraction method after nitrogen and phosphorus were adsorbed.

Untreated bamboo powder showed minimal leaching of total nitrogen or magnesium. The major form of nitrogen was ammonia. Phosphate and potassium oxide also showed leaching of about 2 mg/g. In the Mg bamboo experiment, 1.5 mg of nitrate and 3.6 milligrams of magnesium oxide were extracted per gram, suggesting a link to the adsorption process. The results are further contextualized by examining the results of oyster shells used as adsorbents in both nitric acid alone and in a mixed solution of nitric acid and phosphoric acid. These adsorbents were then extracted with citric acid. The former showed 4 mg/g of nitric acid, and the latter 2 mg/g. Phosphate was detected in both, but at higher concentrations in the adsorbent used in the mixed solution. The results confirm that the expected components were effectively adsorbed on the intended adsorbents.

4. Conclusions

The conclusions of this study are as follows:

Three types of biomass were used as raw materials, and their adsorption of nitrate ions was investigated. Adsorption was carried out using bamboo meal, which was passed through a 178 µm sieve and treated with magnesium chloride to increase the adsorption capacity. The adsorption method was a mixture of multilayer physisorption (Freundlich) and single-layer chemisorption (Langmuir), and was estimated to be 399 mg/g by the D-R method (correlation coefficient: 0.84). Citric acid extraction of the adsorbent resulted in the detection of nitric acid in the extract. Multi-layer physisorption was suitable for oyster shells; the maximum adsorption was estimated to be 354 mg/g by the D-R adsorption equation (correlation coefficient: 0.94). The adsorbed nitric acid could be extracted with citric acid. When hydrogelation was used to solve the separation problem, only multilayer physisorption or the D-R formula was suitable, with a correlation coefficient of 0.994 and a maximum adsorption of 156 mg/g by the D-R method. Only the hydrogel was able to detect nitrogen as an element in the EDS analysis.

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