Research article

Recycling of Nitrogen and Phosphorus from Urban Wastewater Using Calcium-Silicate-Hydrate: A Case Study in Cambodia

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Abstract The main goal of this research study was to evaluate the calcium-silicate-hydrate (CSH) synthesized from calcium hydroxide ($Ca(OH)_2$) and rice husk charcoal and to determine if the CSH is economically and environmentally friendly and can be used as a promising strategy for nitrogen and phosphorus recovery. The CSH material was prepared by combining $Ca(OH)_2$ and rice husk charcoal in a 1:4 ratio and mixing the sample with 75% deionized water. Following mixing, a vibrator was used for 1 minute for Case 1, 2 minute for Case 2 and 3 minute for Case 3. The CSH was then put into molds which were maintained at room temperature for 3 weeks before starting the experiments. The two weeks adsorption experiment investigated parameters such as pH, EC, Ca, K, NH_4^+, and PO_4^{3-} in 2 weeks. The 1st and 2nd elusion experiments were carried out on used CSH to test the dissolution rate of NH_4^+ and PO_4^{3-}. To confirm the used CSH effectiveness as a fertilizer, a plant growth experiment was also carried out to measure the growth rate of spinach and the improvement of soil fertility. The results of the adsorption experiment indicated that CSH can effectively remove nutrients from wastewater, achieving removal rates of 97% for NH_4^+ and 98% for PO_4^{3-}. The adsorption capacity of CSH is 0.065 mg-NH_4^+/g-CSH and 0.11 mg-PO_4^{3-}/ g-CSH. Additionally, the used CSH can release 3-5 mg/kg for NH_4^+ and 6.6-7.7 mg/kg of PO_4^{3-} in the elusion experiments. Moreover, the plant growth experiment also indicates that the soil fertility increased 3 times with the 5% addition of used CSH treatment, compared to the control treatment. These results suggest that CSH, made from $Ca(OH)_2$ and rice husk charcoal, could serve as a cost-effective solution to wastewater treatment and production of fertilizer for agricultural production.

Keywords CSH, dissolution fertilizer, Phosphate, Ammonium, plant growth

INTRODUCTION

Cambodian urbanization has led to environmental problems, especially water pollution. Water degradation has been reported near the discharge point of the Phnom Penh city into the Mekong River (Chea et al., 2016).Research has been done to assess the water quality in Cheung Ek Lake which found excess nutrient content (Samuel et al., 2019). As recently as ten years ago, this lake was known for its natural wastewater treatment capacity to remove the nutrients from the lake's water, including a 22% and 67% reduction for total nitrogen (TN) and total phosphorus (TP), respectively (Visoth et al., 2010). Most natural lakes typically possess the capability for self-purification; however, this process requires time, with nitrification typically requiring 2-6 weeks. However, as Cheung EK lake's area decreases by half (Kawamura et al., 2015; Ro et al., 2020), the hydraulic retention time in the lake also diminishes, resulting in a reduction or loss of the lake's wastewater treatment capacity. Hence, there is a necessity to find additional new methods to improve the water quality. Low-cost and high-performance materials or techniques that could synergistically remove pollutants in a simple manner are highly desired.

Manmade wastewater treatment methods are summarized into 5 main categories: adsorption, membrane, chemical, electric, and photocatalytic. (Qasem et al., 2021). Given that Cambodia is a developing country, the adsorption method was adopted in this study because of its cost-effectiveness and being environmentally friendly. The adsorption-based method has been widely studied and its benefits and costs discussed (Vievard et al., 2023; Araujo et al., 2018) but only calcium silicate hydrate (CSH) can remove the pollution from water and be used as fertilizer (Lee et al., 2018). Although previous studies evaluated the use of CSH for pollutant removal and as a fertilizer, the initial material and process of manufacturing CSH were different from one to another, leading to differences in capacity and effectiveness. Therefore, this paper will highlight the CSH production method that is applicable to Cambodia.

This research endeavors to identify the simplest, and most suitable method to produce CSH, such as with a material like rice husk and calcium hydroxide. Rice husk is the principal agricultural waste product generated during rice processing and it is known for its effectiveness in the removal of pollution in water (Okoro et al., 2022). In Cambodia, the Food and Agriculture Organization (FAO) reported in 2022 that the country produces approximately 11.6 million tons of rice annually, generating 2.3 million tons of rice husk each year (FAO, 2023). Simultaneously, calcium is readily accessible in Cambodia due to calcium mining, rendering calcium hydroxide affordable for farmers at a price of USD 300 per ton. This new use of rice husks will directly contribute to decreasing agricultural waste and allowing farmers to produce their own fertilizer for application to their farmland soil.

OBJECTIVE

The objectives of this research study were to propose a new method for simplifying the synthesis of CSH, assessing its performance, and determining if it should be presented as an economically and environmentally friendly strategy for wastewater treatment.

METHODOLOGY

Preparation for CSH

CSH material was synthesized from $Ca(OH)_2$ and rice husk charcoal (RHC). This experiment utilized commercially available products with a purity of ≥ 99%. First RHC was crushed to powder form, then mixed with $Ca(OH)_2$. The resultant mixture of CSH was the mass-based ratio of $Ca(OH)_2$:1 and RHC:4 and 75% deionized water was added for the hydration reaction. After mixing, it was processed with a concrete vibrator for 1 minute for Case 1, 2 minutes for Case 2 and 3 minutes for Case 3 (Fig. 1). Scanning electron microscope (SEM) images of the CSH are shown in Fig. 2, revealing an agglomeration of crystalline particles with rough surfaces. Pores become smaller with an increase in the vibration time from 1 to 3 minutes.

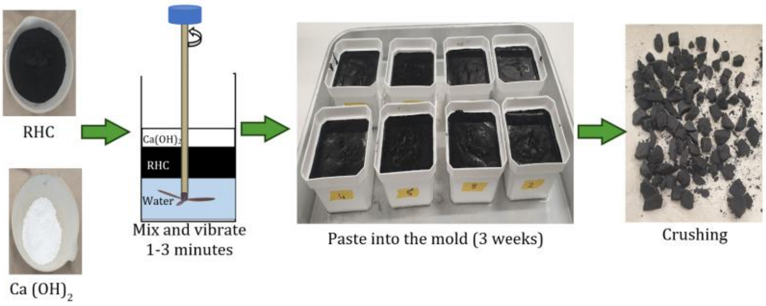

Fig. 1 Processes of CSH preparation

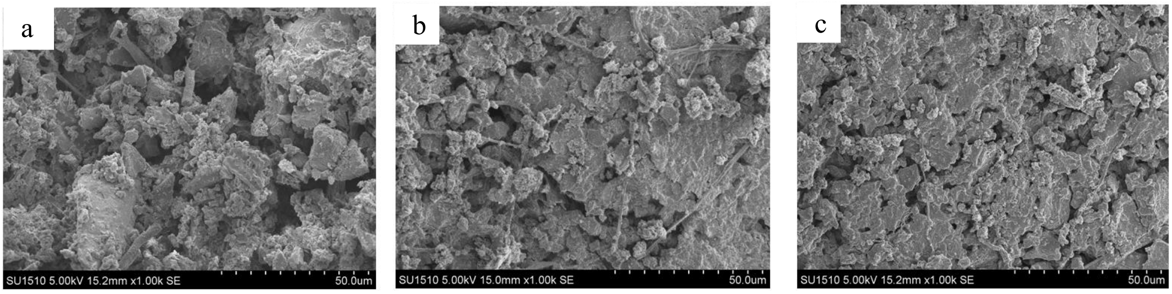

Fig. 2 SEM images of the CSH sample

(a) 1 minute (b) 2 minutes and (c) 3 minutes of vibration 1,000x magnification

Preparation for Adsorption Experiment

A total of nine samples were used in the adsorption experiment, with three samples from each of Case 1, Case 2 and Case 3. The 4 g of CSH materials (1 minute, 2 minute, and 3 minutes vibration) were immersed in 40 mL of deionized water (maintained at 21ºC) for 3 hours to test for the dissolution components from CSH (Table 1). Upon immersing the CSH in deionized water, a consistent increase in pH levels from 7 to 12 was observed across all cases in 3 hours. When water is added to cement, the calcium silicate phases, primarily tricalcium silicate (C3S) and dicalcium silicate (C2S) begin to dissolve, releasing calcium ions and silicate ions into the solution (Blanc et al., 2010). This dissolution explains the high concentration of calcium ions released into the water, resulting in elevated pH levels. This explains the high concentration of calcium ions released into water and leads to high pH as well. The low concentration of silicate ions observed could be because, upon release during hydration, the silicate ions reacted immediately and were swiftly incorporated into the forming C-S-H structure.

Table 1 Dissolution components from produced CSH

Case	pH	EC (mS/m)	Ca (mg/L)	K (mg/L)	Si (mg/L)
Case 1	12.03	121.7	300	3	5.8
Case 2	12.09	79	270	1	6.9
Case 3	12.28	103	390	2	3.4

After the dissolution test, the CSH was air-dried for 1 week to eliminate the access water and then soaked again in 20 mL of wastewater for 14 days to test nutrient removal capacity. The initial condition of wastewater is indicated in Table 2.

Table 2 Initial conditions of wastewater

Solution	pH	EC (mS/m)	Ca (mg/L)	K (mg/L)	NH_4^+ (mg/L)	PO_4^{3-} (mg/L)
Wastewater	6.60	55.0.5	31.5	160	13.4	23.4

Evaluation of Ammonium and Phosphate Recovery Performance

The amount of adsorbed ammonium and phosphate at time t (Q_t: mgNH_4^+/g) and (Q_t: mgPO_4^{3-}/g) was calculated as the difference between concentrations in solution initially (C_i: mgL^{-1}) and at time t (C_t: mgL^{-1}) using the following Eqs. (1)

$$Q_t = (C_i - C_t)\ V / W \tag{1}$$

Where V is the volume of solution L and W is the dry mass of adsorbents (g). The nutrient removal rate (RE) was calculated using Eq. (2).

$$\%\ RE = [(C_i - C_e)/Ci] \times 100 \tag{2}$$

Preparation for an Elusion Experiment

The elusion experiment was conducted to assess the potential of used (nutrient-adsorbed) CSH as fertilizer. The used CSH that was obtained from the adsorption experiment was air dried for 1 week and placed in the deionized water for 24 hours to measure the release of the NH_4^+, and PO_4^{3-}. Using the same process utilized for the first elusion test, the 2nd elusion test was conducted the second time release of the NH_4^+, and PO_4^{3-} from the used CSH material.

Preparation of Plant Growth Experiment

Pot experiments are controlled studies used to investigate plant growth and soil processes, complementing field measurements (Kawaletz et al., 2014). In this study the pots experiment was conducted in the summer of 2022 in the land and water use engineering laboratory of Tokyo University of Agriculture at the temperature 20^0C-25^0C with 2 treatments: control treatment (without CSH) and CSH treatment (5% of used CSH).

To enhance germination, spinach seeds underwent pretreatment by soaking in warm water at 55-60 ℃ for 15 minutes (Yuan et al., 2022). After pretreatment, the seeds were directly planted in pots, with each pot containing six seeds. Two weeks after planting, water was evenly irrigated at a rate of 20 mL every three days. Artificial light was consistently supplied 24 hours a day throughout the entire duration of the plant growth experiment. The height of the spinach was observed and measured in three-day intervals from the one week until one month. After one month, the spinach was harvested and measured for plant weight, leaf area and stem height. The plant area growth was determined using Image J.

RESULTS AND DISCUSSION

Ammonium and Phosphate Removal by of CSH

Figure 3 illustrates the average results of 1 to 3-minute vibration for CSH. On Day 1, the removal rate for NH_4^+ was 27%, gradually increased to 97% by Day 7 and remained stable until the end of the experiment (Day 14). Similarly, for PO_4^{3-}, the removal rate starts at 45% on Day 1, gradually increased to 98% on Day 7, and was stable until Day 14. The phosphate and ammonium adsorption capacity of CSH was 0.11 PO_4^{3-}-mg/g-CSH, and 0.065 NH_4^+-mg/g-CSH. However, the capacity observed in this experiment should not be taken as the definitive maximum capacity of the CSH. Additional experiments are necessary to ascertain its upper capacity limits, as the current findings are based on a single experimental result. The adsorption of NH_4^+ and PO_4^{3-} was lower than that of activated carbon (29 mg-N/g, 14.1 mg-P/g) and bio-adsorbent (45 mg-N/g, 12 mg-P/g) (Vassileva et al., 2009; Wang et al., 2012; Yadav et al., 2015; Kizito et al., 2015).

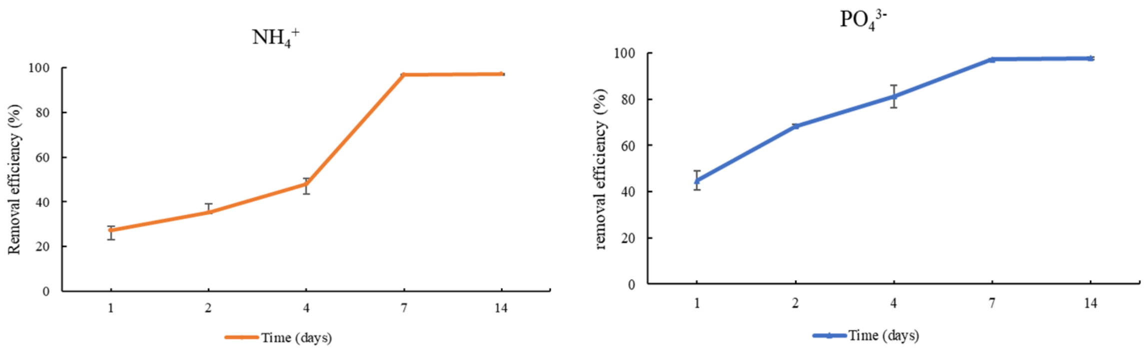

Fig. 3 Average removal efficiency of ammonium and phosphate by CSH

The variation in absorbent rates can be primarily attributed to the physical properties of CSH, characterized by its macroporous structure, in contrast to activated carbon and biochar, which exhibit a micro-mesoporous type of configuration. From SEM image in Fig. 2 confirmed that CSH derived from rice husk charcoal and calcium dioxide had macropores with an average of 50-100 µm and high porosity, which led to a lower specific surface area. The micro-mesoporous type possesses a larger specific surface area, enabling it to effectively absorb ions to a greater extent compared to structures with larger pores. Furthermore, according to Kizito et al. (2015), the optimal pH range for adsorption is 4-8. In this experiment, the CSH was eluted at a high pH (11-12) in the solution during the adsorption process, which affected its removal capacity.

Release of Ammonium and Phosphate from Used CSH

This CSH exhibits a unique characteristic in its ability to elute back nutrients without additional activators, a feature that is not present in other absorbent materials.

The elution test was carried out to assess the amount of ammonium and phosphate that could be released from used CSH in deionized water without any additional pre-treatment, such as pH adjustment. In Figure 4 (a) and (b), CSH exhibited the release of ammonium ranging from 3-5 mg-NH_4^+/kg-CSH and 6.6-7.7 mg-PO_4^{3-}/kg-CSH during 3 hours of elution. The reduction of phosphorus concentration at 24 hours (Fig. 4b) due to the presence of Ca^{2+} ion in the solution, which led to the formation of calcium phosphate ($Ca_3(PO_4)_2$). Under neutral or alkaline conditions, direct precipitation $Ca_3(PO_4)_2$ and $Ca_5(PO_4)_3OH$ are readily achieved most likely follow as Eqs.

$$5Ca^{2+} + 3HPO_4^{2-} + 4OH^- = Ca_5(PO_4)_3OH + 3H_2O \quad (3)$$

$$3Ca^{2+} + 2HPO_4^{2-} + 2OH^- = Ca_3(PO_4)_2OH + 2H_2O \quad (4)$$

Where increases in OH^- allow the chemical precipitations to occur more readily, resulting in higher removals. However, a large excess of OH^- would appear to impair $Ca_5(PO_4)_3OH$ precipitation allowing a dissolution back into solution with increased reaction times (Kim et al., 2020). The results of the second elution test demonstrate a sustained release of ammonium and phosphate into the deionized water over a period of 3 hours, followed by a subsequent decrease within 24 hours.

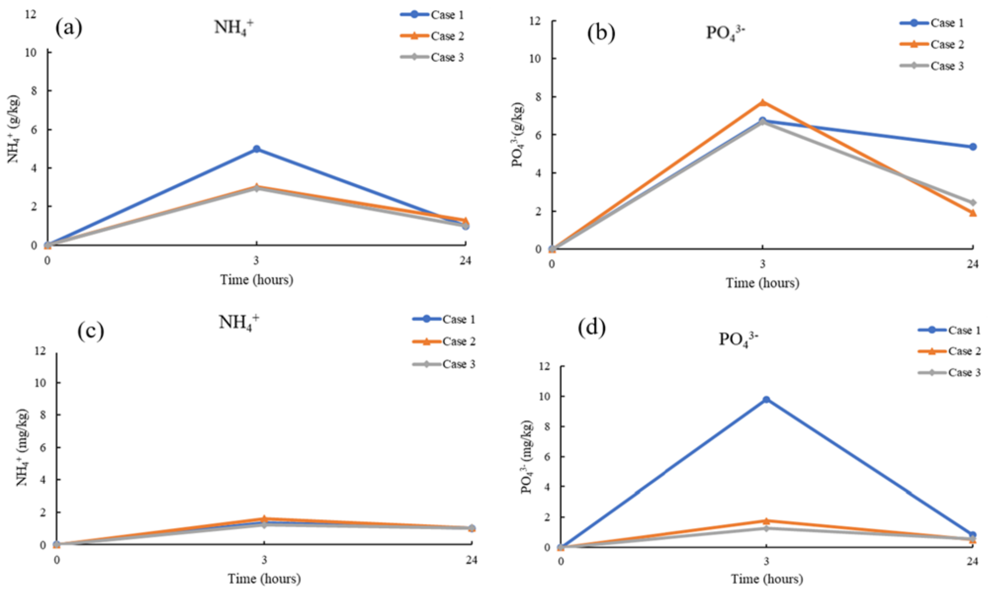

Fig. 4 Release of NH_4^+ and PO_4^{3-} from used CSH

First elution test (a), (b) and Second elusion (c), (d)

This pattern aligns with the observations from the first elution test. Nevertheless, in the second elution test, Case 1 exhibited the highest rate compared to the other cases, suggesting that CSH with 1 minute of vibration is optimal for release capacity, likely attributed to its high porosity. In contrast to commercial chemical fertilizers, this CSH exhibits a gradual release of nutrients, making it highly suitable for application in farmland soil as a fertilizer.

Plant Growth Changes with Adding Used CSH

Figure 5 illustrates the comparison between the control and CSH treatment in terms of spinach plant growth. The results indicate a significant impact of the CSH treatment on height, root development, leaf length, and leaf width. Similarly, in Table 3, the soil fertility with a 5% addition of used CSH shows a threefold increase in nitrogen (N), phosphorus (P), and potassium (K) compared to the control. The findings from these results suggest that used CSH can serve as a viable alternative fertilizer to chemical fertilizers in agricultural production.

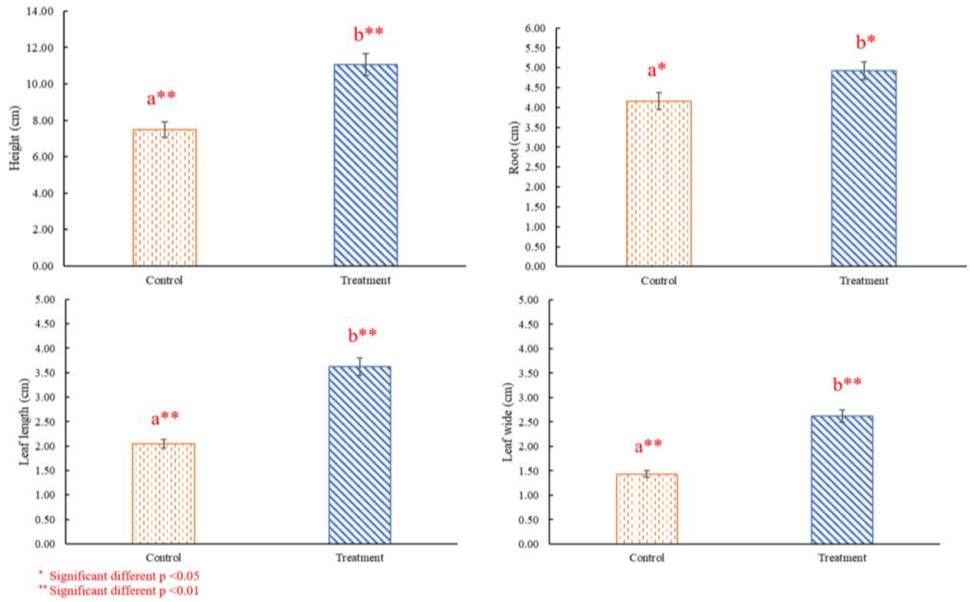

Fig. 5 Effect of used CSH on spinach plant growth

Table 3 Effect of CSH on soil fertility

Treatment	pH	EC (µS/cm)	N (mg/kg)	P (mg/kg)	K (mg/kg)
Control	5.58	120.88	9.33	13.17	26.83
CSH treatment	7.78	411.17	29.00	40.33	81.50

CONCLUSION

This study aimed to deal with the development of CSH and evaluate its capacity for nutrient removal from wastewater and its ability to be used as fertilizer. The findings demonstrated that CSH synthesized from calcium hydroxide ($Ca(OH)_2$) and rice husk charcoal can efficiently absorb 98% of PO_4^{3-} and 97% of NH_4^+.The adsorption quality was 0.11 mg-PO_4^{3-} /g-CSH and 0.065 mg-NH_4^+ /g-CSH. In the 1st elution experiments, the used CSH can release 3.23 mg/kg for NH_4^+ and 7.05 mg/kg for PO_4^{3-}. NH_4^+ and PO_4^{3-} were also observed to continue to be released in the second experiment. The outcomes of the spinach plant growth experiment, where used CSH was applied as a treatment, demonstrated enhanced growth rate of the height, root, leaf length and leaf width, accompanied by a threefold improvement in soil fertility (N, P and K). The distinctive feature of this CSH lies in its requirement for only two components, namely calcium hydroxide ($Ca(OH)_2$) and rice husk charcoal. The manufacturing process is straightforward, devoid of the need for any additional treatment or activator, making it easily adaptable for farmers. In conclusion, it can be inferred that CSH is effective in the removal of nutrients, particularly NH_4^+ and PO_4^{3-}. Additionally, according to the results of this study, CSH has the potential to be a viable substitute for commercial chemical fertilizers in agricultural production. However, additional economic analysis research needs to be conducted to verify the potential and assess the real market value of the CSH.

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