# An Investigation on the Phosphorus Removing Capacities of Calcined Eggshells and Woodchips

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## Introduction

Eutrophication

- Excessive phosphorus accumulation due to fertilization on agricultural land has raised concerns of the eutrophication of surrounding bodies of water *(1)*

**Figure 1.** Green algae bloom on Breton beach (2)

- Many dephosphorization techniques have been studied and evaluated for their effectiveness, economic strain, and environmental consequences
- Among different techniques, adsorption have been identified to be lower cost, easier to manipulate and simpler in design *(3)*

Calcined Materials

- One of the newer approaches to phosphorus adsorption is using waste materials and agricultural by-products *(4)* as it is environmentally conscious and cost-efficient
- Calcinated eggshells are characterized by a porous nature, and high $CaCO_3$ content that provide means of phosphorus removal through the formation of hydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2]$ *(5)*
- With similar $CaCO_3$ concentrations, the investigations on oyster and mussel shells have also demonstrated promising results with P adsorption greater than 80% when shells are calcined *(3)(6)(7).*

## Research Objectives

- The objective of this investigation was to characterize the phosphorus removal ratios of calcined eggshells mixed with a secondary substrate suitable to be integrated in a bioreactor to be employed at on-site locations of farmlands
- Extensive literature reviews were conducted prior to experimentation. Review was used to identify two potential secondary substrates to be used.
- Secondary substrates identified as non-calcinated eggshells due to their accessibility and previous use in similar investigations *(5)* and woodchips due to their denitrifying properties in previous investigations *(8)*
- The preliminary experiments identified which secondary substrate resulted in the greatest phosphorus removal when mixed with calcinated eggshells
- Secondary experiments identified the ideal pH for the reactions to proceed, and the third set of experiments attempted to characterize the ideal phosphorus concentration for the reaction to proceed

## Methods

### Question 1: Which secondary substrate results in the greatest phosphorus removal and at what mass ratio?

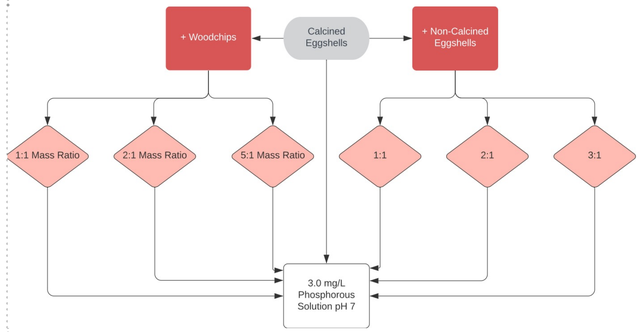


**Figure 3.** Protocol for identifying ideal secondary substrate and mass ratio

**Table 1.** Mass breakdown for mixtures of primary and secondary substrate

| Primary Substrate (mg) | Secondary Substrate (mg) | Ratio |
|---|---|---|
| 120 | 120 | 1:1 |
| 160 | 80 | 2:1 |
| 200 | 40 | 5:1 |

Phosphorus (P) removal ratio (R%) will be calculated based on the equation:

$$R[\%] = \frac{C_0 - C_e}{C_0} \cdot 100\% \quad [1]$$

Where $C_0$ and $C_e$ are initial and equilibrium P concentration mg/L. Equation will be used for all investigative questions.

### Question 2: What is the optimal pH for phosphorus removal?

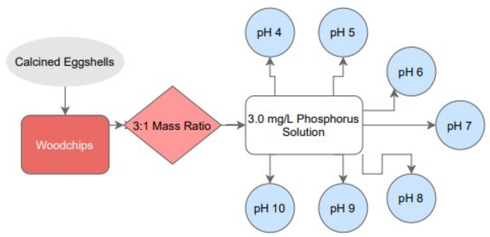


**Figure 4.** Protocol for identifying ideal pH

## Methods cont.

### Question 3: What phosphorus concentration results in greatest phosphorus adsorption?

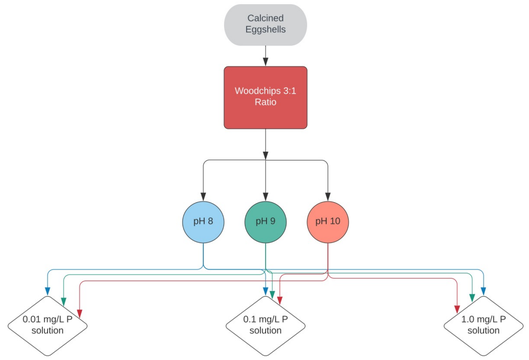


**Figure 5.** Protocol for identifying ideal P concentration

## Results

**Answer 1:** Ideal secondary substrate found to be woodchips at 5:1 ratio. 2:1 CE:WC demonstrated P removal >60% after 2 hours. 3:1 ratios employed in further investigative questions.

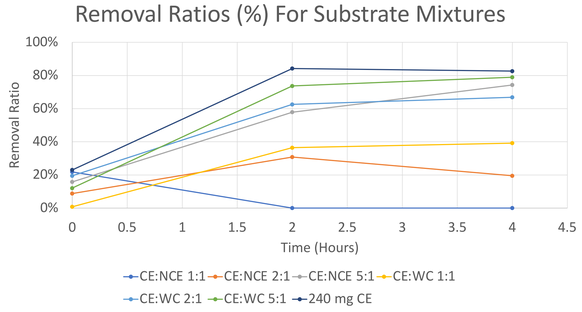


**Figure 6.** P Removal Ratios for substrate mixtures of calcinated eggshells (CE) and woodchips (WC) or CE and non calcinated eggshells (NCE).

**Answer 2**: pH values greater than 7 displayed greatest P removal

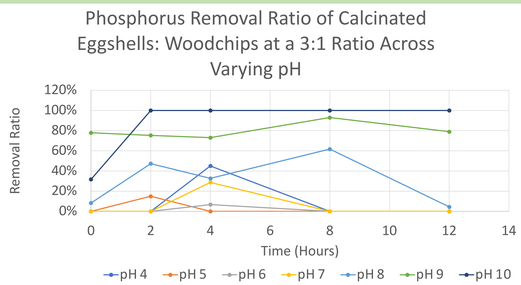


**Figure 7.** P Removal across pH 4-10 over 12 hours

## Results cont.

**Answer 3:** No clear consensus on optimal P concentration

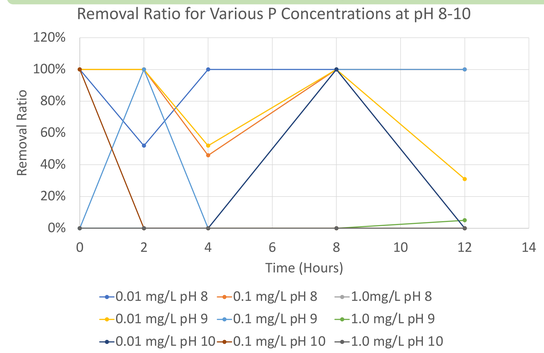


**Figure 8.** P removal across P concentrations 0.01-0.1 mg/L over 12 hours

## Conclusion

- Results from preliminary tests indicated that woodchips as a secondary substrate in a 5:1 ratio with calcinated eggshells results in P removal similar to that of pure calcinated material
- Results of secondary tests indicated an optimal pH range of 8-10 which coincides with previously conducted investigations
- No clear consensus on ideal P concentrations however removal ratios for P concentrations of 3.0 mg/L from preliminary and secondary tests demonstrated P removal > 60% for 3:1 CE:WC at pH 7, and > 60% for pH 9, 10.

## Next Steps

- Langmuir and Freundlich isotherm models will be employed using the removal ratios calculated in this investigation
- Models will be used to determine the maximum sorption capacity of substrate mixtures
- The findings will be used in the development of an on-site bioreactor to be used on agricultural land

## References

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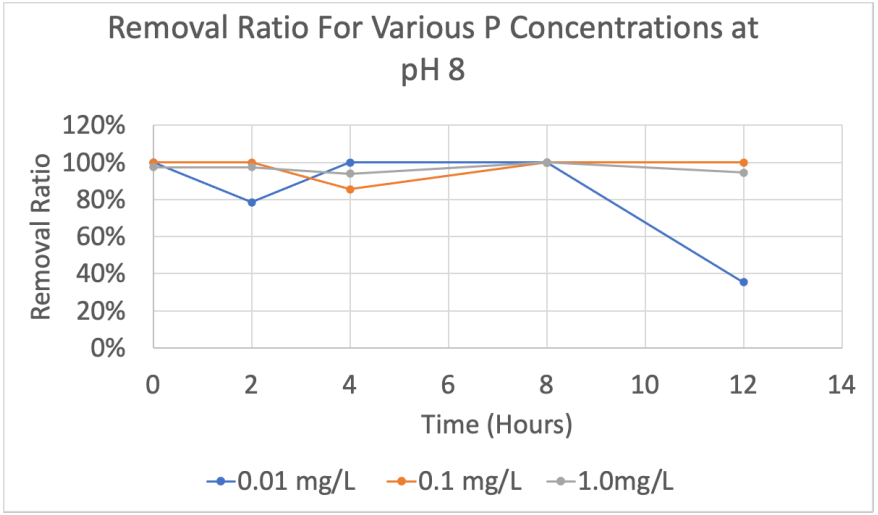
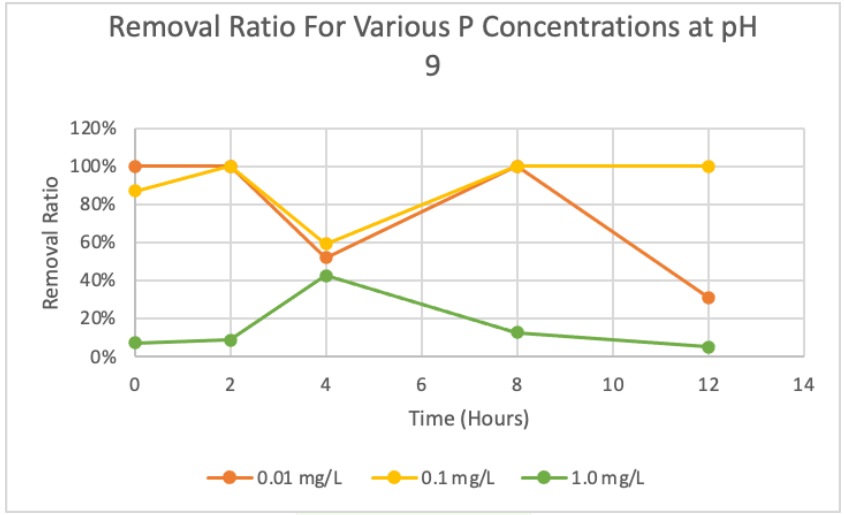
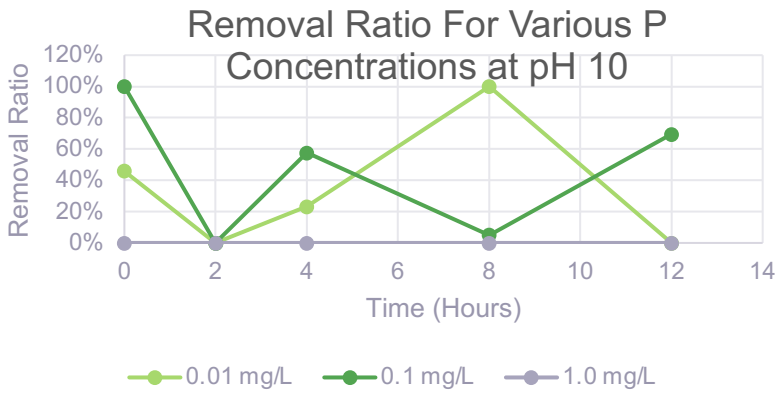

Removal Ratio For Various P Concentrations at pH 8
120%
100%
80%
60%
40%
20%
0%
Removal Ratio
0
2
4
6
8
10
12
14
Time (Hours)
0.01 mg/L
0.1 mg/L
1.0mg/L


Removal Ratio For Various P Concentrations at pH 9
120%
100%
80%
60%
40%
20%
0%
Removal Ratio
0
2
4
6
8
10
12
14
Time (Hours)
0.01 mg/L
0.1 mg/L
1.0 mg/L


Removal Ratio For Various P Concentrations at pH 10
120%
100%
80%
60%
40%
20%
0%
Removal Ratio
0
2
4
6
8
10
12
14
Time (Hours)
0.01 mg/L
0.1 mg/L
1.0 mg/L

# Formation of Hydroxyapatite

$$CaCO_3 + heat \rightarrow CaO + CO_2 \quad [1]$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad [2]$$

$$10\,Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O \quad [3]$$