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)
- Many dephosphorization techniques have been studied and evaluated for their effectiveness, economic strain, and environmental consequences
- Among different techniques, adsorption has 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
- Calcined eggshells are characterized by a porous nature, and high CaCO₃ content that provide means of phosphorus removal through the formation of hydroxypatite [Ca₅(PO₄)₃(OH)] (5)
- With similar CaCO₃ 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 1. Green algae bloom on Breton beach (2)](image)

![Figure 3. Protocol for identifying ideal secondary substrate and mass ratio](image)

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

<table>
<thead>
<tr>
<th>Primary Substrate (mg)</th>
<th>Secondary Substrate (mg)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>120</td>
<td>1:1</td>
</tr>
<tr>
<td>160</td>
<td>80</td>
<td>2:1</td>
</tr>
<tr>
<td>200</td>
<td>40</td>
<td>5:1</td>
</tr>
</tbody>
</table>

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

\[ R(\%) = \frac{C_0 - C_2}{C_0} \times 100\% \quad [1] \]

Where C₀ and C₂ 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](image)

![Figure 5. Protocol for identifying ideal P concentration](image)

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

![Figure 6. P Removal for substrate mixtures of calcinated eggshells (CE) and woodchips (WC) or CE and non calcinated eggshells (NCE).](image)

Results

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

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

Answer 3: No clear consensus on optimal P concentration for various P concentrations at pH 4-10.

![Figure 8. P removal across P concentrations 0.01-0.1 mg/L over 12 hours](image)

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 the substrate mixtures
- The findings will be used in the development of an on-site bioreactor to be used on agricultural land

References

Removal Ratio for Various P Concentrations at pH 8

- 0.01 mg/L
- 0.1 mg/L
- 1.0 mg/L

Removal Ratio For Various P Concentrations at pH 9

- 0.01 mg/L
- 0.1 mg/L
- 1.0 mg/L

Removal Ratio For Various P Concentrations at pH 10

- 0.01 mg/L
- 0.1 mg/L
- 1.0 mg/L
Formation of Hydroxyapatite

\[ \text{CaCO}_3 + \text{heat} \rightarrow \text{CaO} + \text{CO}_2 \]  \quad [1]

\[ \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \]  \quad [2]

\[ 10\text{Ca(OH)}_2 + 6\text{H}_3\text{PO}_4 \rightarrow \text{Ca}_{10}\text{(PO}_4)_6\text{(OH)}_2 + 18\text{H}_2\text{O} \]  \quad [3]