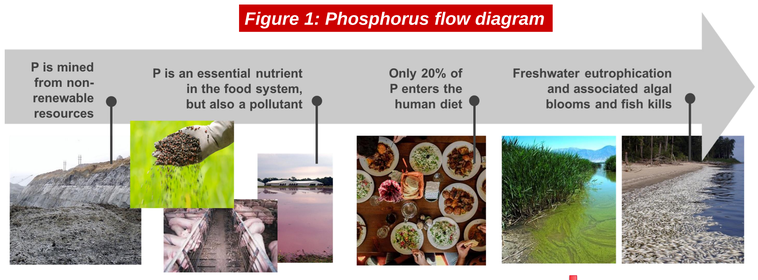
Investigating Metal-Cation-Containing Materials for Efficient Phosphorus Capture and Recovery

Darrell Ifiok Harry[1,2], Manuel Gonzalez Abrego[3], Detlef Knappe[2,4], Jacob L. Jones[1,2]

[1]Department of Materials Science and Engineering, North Carolina State University, [2]Science and Technologies for Phosphorus Sustainability Center, North Carolina State University, [3]Ravenscroft School, [4]Department of Civil, Construction, and Environmental Engineering, North Carolina State University

Introduction

Figure 1: Phosphorus flow diagram



- Phosphorus (P) is a critical, limited resource essential for global food supply.
- P-discharge from agricultural runoff and wastewater threatens aquatic ecosystems by causing eutrophication and harmful algal blooms.
- Metal-cation-containing materials like oxides, hydroxides, and carbonates have significant potential for P-capture, making them promising for commercial and industrial P-recovery applications.
- Adsorption and Dissolution-precipitation have been determined to be the main mechanism of P-capture by Metal-cation-containing materials.

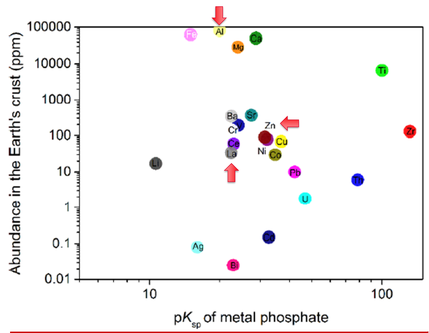
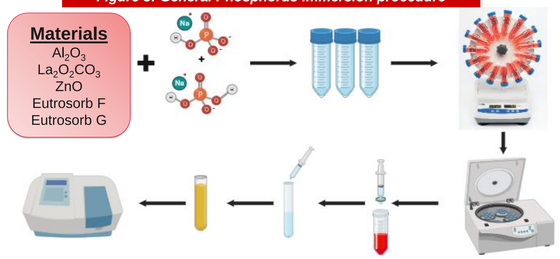


Figure 2: Metal abundance in the Earth's crust and solubility product constant (pK_{sp}) of the metal-phosphate.[1]

- Systematic studies are needed to investigate the fundamental relationship between the structure-composition-property and P-capture ability of these materials using consistent theoretical and experimental techniques.
- Thus, this study methodically evaluates the potential of materials containing popularly used metal cations like Al^{3+}, Ca^{2+}, Fe^{3+}, Mg^{2+}, K^{+}, La^{3+} and Zn^{2+} for P-capture and recovery.

Methods

Figure 3: General Phosphorus immersion procedure



- Materials are immersed in 25 mL of NaH_2PO_4 and Na_2HPO_4 solution at pH 7, with varying initial phosphorus concentrations and a fixed sorbent dosage for 24 hours.
- The mixture is rotated at a constant speed for 24 hours, then centrifuged to separate solids from the liquid.
- For **Phosphorus capture** analysis, the liquid is mixed with a Molybdovanadate reagent, forming a yellow color upon reaction with unbound phosphorus. After 7 minutes, the absorbance is measured at 420 nm using a spectrophotometer to determine the concentration of unbound phosphorus, allowing for calculation of the captured phosphorus.
- The solid material is dried and analyzed using **X-ray Diffraction** to determine the mechanism of P-capture by the material by analyzing any structural changes.
- **Phosphorus selectivity** of the materials is assessed by adding sodium salts of ions such as Cl^-, F^-, HCO_3^- NO_3^- and SO_4^{2-} to the solution of P at 10 and 20 times the normality of PO_4^{3-}.
- **Phosphorus desorption** is analyzed by an immersion of the materials after they've been used to capture P in 25 mL of 0.1 M NaOH for 24 hours to release the bound P.
- The performances of the materials studied here are also compared to two commercial products currently on the market that are used to capture P, Eutrosorb F and Eutrosorb G (a 10% La modified bentonite material).

Figure 4: Rigaku Diffractometer

Results

Figure 5: Phosphorus capture

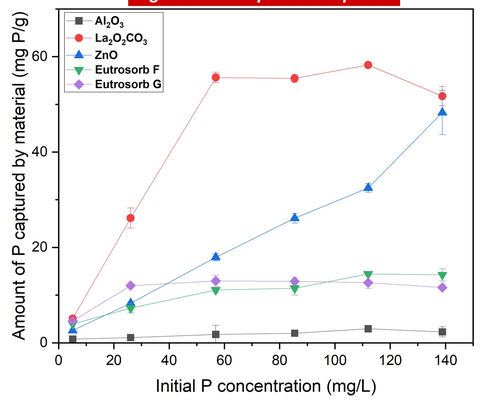


Figure 6: Phosphorus selectivity

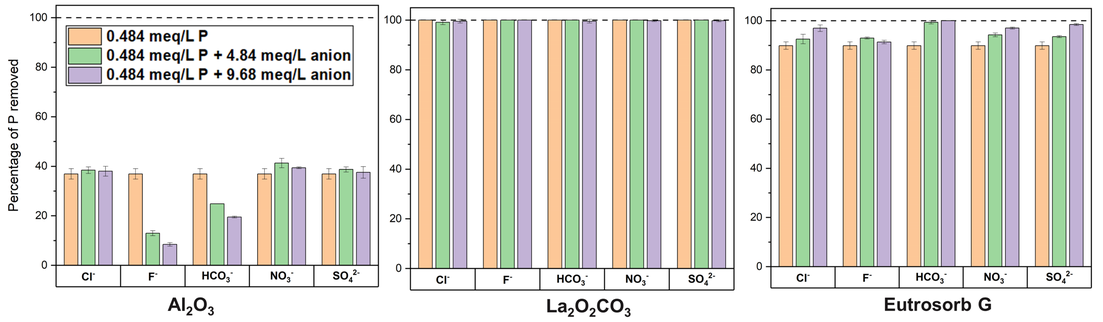


Figure 7: Phosphorus desorption

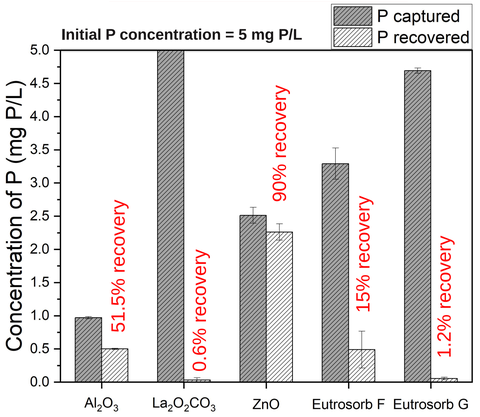
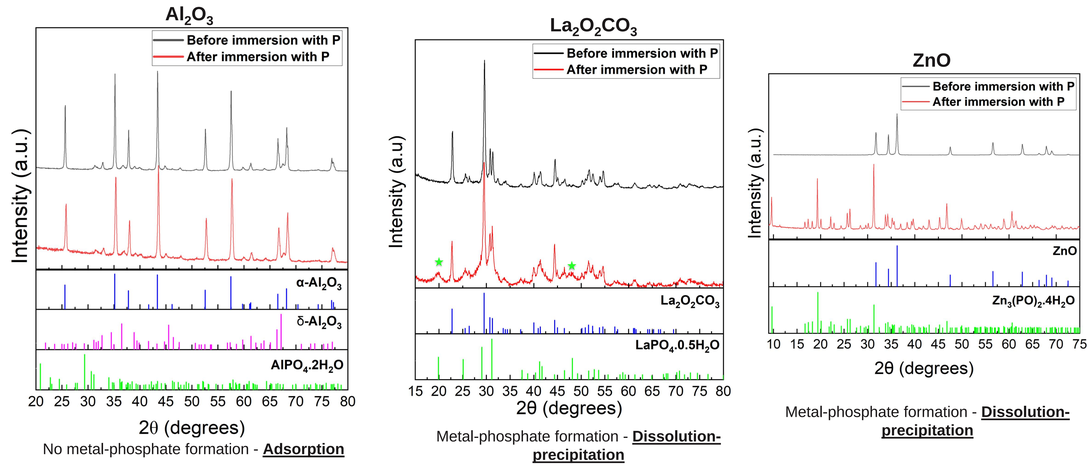


Figure 8: X-ray diffraction before and after immersion with Phosphorus



Discussion

- $La_2O_2CO_3$ effectively captures P across various concentrations, with 1 mg removing 2.2 mg of P. It captures P through partial dissolution precipitation by releasing La^{3+} in solution which binds with P to form nanocrystalline $LaPO_4.0.5H_2O$ (rhabdophane). It shows high selectivity for phosphate over competing ions and has low ecotoxicity. However, Its poor P desorption limits reusability.
- ZnO is a mid-tier P-capture material, with 1 mg removing 2 mg of P across various concentrations. It selectively binds P through dissolution, forming a $Zn_3(PO_4)_2{\cdot}4H_2O$ complex, most likely through a seeding process and is unaffected by interfering ions. It has excellent desorption, removing over 90% of captured phosphate, making it reusable. However, it poses ecotoxicity risks at high concentrations, potentially harming aquatic life and bioaccumulating in organisms.
- Al_2O_3 is a poor P-capture performer, removing P through adsorption. Its selectivity towards P decreases in the presence of F^- and HCO_3^- and poses ecotoxicity risks to humans and aquatic life at high concentrations. However, it can desorb over 50% of captured P, indicating some reusability.
- The commercial products have mid-tier P-capture performances across different initial P concentrations. Eutrosorb G behaves similarly to $La_2O_2CO_3$ in that it is not affected by the influence of other competing cations and is enhanced by them and poorly desorbs P. Eutrosorb F's performance on the other hand was affected by the influence of competing ions, decreasing with increasing ion concentration.
- This study effectively highlights the diverse P-capture and recovery behaviors of various metal-cation-containing materials. Future work will test P-capture in real wastewater containing organic matter. ICP-OES will be used to measure metal ion leaching from materials in solution. Higher concentrations of NaOH (1 M) will be used to improve desorption. Other materials characterization techniques like FTIR, SEM/EDS, and XPS will characterize materials pre- and post-P capture and release.
- The key takeaway is that the diverse P-capture and recovery properties of these metal-cation-containing materials allow for varying end uses, from single-use to multiple-use applications.
- Materials with ecotoxicity concerns need modification to prevent leaching while retaining P-binding capability.

References

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