

Zirconium Phosphate and Phosphonate Nanoparticles for Phosphate Removal from Water: An Aquarium Life Support System Application

Adam M. Ross, Monique N. Williams, Daniel R. Talham and Jeffrey J. Keaffaber*
University of Florida
Department of Chemistry

Abstract

In aquatic environments, phosphorus is known as the “limiting nutrient.” It combines with nitrogen and photosynthetic processes to produce plant and algal growth. Phosphorus in marine life support systems exists in either a particulate or dissolved phase. While particulate sources may be removed during filtration or fractionation, the dissolved form persists. In a typical marine environment (pH 8), dissolved phosphorus is almost all hydrogen phosphate ion (HOPO_3^{2-}), also known as inorganic or orthophosphate. Here we report the synthesis and use of zirconium phosphate (α -ZrP, $\text{Zr}(\text{O}_3\text{POH})_2 \cdot \text{H}_2\text{O}$) and zirconium methylenediphosphonate (ZrMDP, $\text{Zr}[\text{O}_3\text{P}(\text{CH}_2)\text{PO}_3]$) nanoparticles for phosphate removal from water. Sodium phosphate solutions (0.5-10.0 mg/L) are exposed to nanoparticle suspensions (10 mg/mL) and phosphate uptake is measured by ion chromatography. In all cases, high phosphate removal is observed. For example, the 5.00 mg/L sodium phosphate solution experiences 99.9% removal after exposure to α -ZrP. After treatment phosphate concentration drops to 0.005 mg/L! This is well below the algal growth threshold (0.01-0.05 mg/L). Future work will explore the particles’ phosphate removal capacity, their regeneration, and the ability to engineer a robust filtration media where the particles are anchored to a silica (sand) surface.

Introduction

Phosphates are common in nature. They exist as the polar hydrophilic head groups in the phospholipid bilayers of cell walls and in micelles. They are also prevalent in nucleic acids (RNA and DNA), and in the cell’s “energy molecule” adenosine triphosphate (ATP). Phosphate minerals in rock like calcium hydroxyphosphate and calcium fluorophosphate are also natural sources.

Phosphorus is dissolved in water primarily as the phosphate ion (PO_4^{3-}). Natural or background concentrations of phosphate in water, also known as inorganic or orthophosphate, are in the range 0.005-0.05 mg/L. Periodic algal blooms may be observed at phosphate concentrations between 0.08-0.10 mg/L. Long term eutrophication can be avoided when phosphate levels are kept below 0.5-0.05 mg/L (Dunne and Leopold, 1978). In marine systems, phosphorus is the

limiting nutrient when the nitrogen to phosphorus ratio is greater than 16, and this is almost always the case in aquarium life support systems. Generally, to minimize algal growth on surfaces, life support and water quality managers try to keep phosphate levels less than or equal to about 0.05 mg/L.

In aquarium life support systems, phosphates are present in particulate and dissolved forms. Particulate phosphorus may be removed during filtration, fractionation, and ozonation processes. Dissolved phosphate remains and circulates through the system. It is this form that is the limiting nutrient for algae growth. At pH 8, about 85% of dissolved phosphate is present as hydrogen phosphate ion (HPO_4^{2-}). The rest is dihydrogen phosphate ion (H_2PO_4^-).

Nanoparticle Systems for Phosphate Sorption

Several groups have studied the structure and morphology of α -ZrP (zirconium phosphate) nanoparticles. They have been synthesized under different conditions to yield particles with varied structure and properties (Sun, et. al., 2007). Gels of zirconium phosphate have been prepared in organic solvents for their use in the preparation of polymer-based nanocomposites (Casciola, et. al., 2005). Glass composite membranes have been impregnated with α -ZrP for use in direct methanol fuel cell applications (Vaivars, et. al., 2004). Intercalation studies where small organic molecules were placed in between individual layers of α -ZrP have also been performed (Wang, et.al., 2006 and Capkova, et. al., 1998).

Two zirconium(IV) nanoparticle materials were synthesized: α -ZrP and ZrMDP. The α -ZrP system, or zirconium phosphate [$\text{Zr}(\text{O}_3\text{POH})_2 \cdot \text{H}_2\text{O}$], was synthesized using zirconyl chloride (ZrOCl_2) and phosphoric acid (H_3PO_4) from known methods (Sun, et.al., 2007). The ZrMDP

system was synthesized by adding $ZOCl_2$ to methylene diphosphonate [$CH_2(PO_3H_2)_2$] (Williams, 2009).

Two sets of three sodium phosphate monobasic ($NaH_2PO_4 \cdot H_2O$ or NaP) solutions were made. The phosphate concentrations were $5.0 \mu M$ (0.48 mg/L), $50 \mu M$ (4.8 mg/L), and $100 \mu M$ (9.6 mg/L). To each set of solutions, 10 mg/mL α -ZrP and ZrMDP was added. The suspensions were stirred for 48 hours, centrifuged, and the supernatant solution was submitted for ion chromatographic analysis (IC). In all cases, except one, the phosphate uptake by the particles was quantitative (100%), an encouraging result! In one solution (4.8 mg/L treated with α -ZrP), approximately 0.005 mg/L phosphate remained by IC integration.

Conclusion

The nanoparticle systems studied here remove all phosphate over a wide range of NaP concentrations. Any phosphate that remains is below IC detection limits.

With this proof of concept in hand, the research will now be directed to three fundamental areas. A phosphate loading study will be designed to determine the maximum uptake capacity of the particles. Second, it will be demonstrated that the particles can be recycled or regenerated using a basic (alkaline) wash, and then reused. Finally, we will engineer a filtration media where the particles will be bonded to silica (sand) and/or polymer bead materials. The goal of this effort is to manufacture a cost effective, robust, and stable material for filter installation.

References

- Dunne, T. and Leopold, L.B. 1978. Water in Environmental Planning, W.H. Freeman and Company. New York.
- Sun, L., Woong, J.B., Sue, H-J., and Clearfield, A. 2007. "Preparation of α -Zirconium Phosphate Nanoplatelets with Wide Variation in Aspect Ratios," *New Journal of Chemistry* 31: 39-43.
- Casciola, M., Alberti, G., Donnadio, A., Pica, M., Marmottini, F., Bottino, A., and Piaggio, P. 2005. "Gels of Zirconium Phosphate in Organic Solvents and Their Use for the Preparation of Polymeric Nanocomposites," *Journal of Materials Chemistry* 15: 4262-4267.
- Vaivars, G., Maxakato, N.W., Mokrani, T., Petrik, L., Klavins, J., Gericke, G., and Linkov, V. 2004. "Zirconium Phosphate Based Inorganic Direct Methanol Fuel Cell," *Materials Science* 10: 162-165.
- Wang, N., Lin, H., Jianbao, L., and Li, X. 2006. "Improved Quasi-solid Dye-sensitized Solar Cell by Composite Ionic Liquid Electrolyte Including Layered α -Zirconium Phosphate," *Applied Physics Letters* 89: 19104.
- Capkova, P., Benes, L., Melanova, K., and Schenk H. 1998. "Structure Analysis of Intercalated Zirconium Phosphate Using Molecular Simulation," *Journal of Applied Crystallography* 31: 845-850.
- Williams, M. 2009. Ph.D. Dissertation, University of Florida