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Fertilizer-Grade Calcium Phosphate Recovery From Wastewater Treatment Plants



ABSTRACT

Phosphorus removal and recovery from wastewater treatment have focused on producing struvite from the gravity belt thickened filtrate through the addition of $Mg(OH)_2$. This study endeavored to improve on this recovery system by producing calcium phosphates from organic acid (OA) digest through the addition of $Ca(OH)_2$ using a fluidized bed reactor (FBR). This study determined that producing calcium phosphates was an efficient recovery system, with 90% P recovery, and could be achieved in less alkaline conditions than those required for struvite. Through X-ray diffraction and computer modeling, it was determined that brushite, a calcium phosphate mineral, was produced.

INTRODUCTION

At present rates of consumption, the world may face P shortages within the next 90 years (Vaccari, 2009). Recovery of P from wastewater treatment plants is one way to extend the supply of virgin P mineral resources. Previous studies (e.g., Le-Corre, 2009) have primarily focused on recovering P as struvite, $NH_4MgPO_4 \cdot 6H_2O$, from the gravity belt thickener (GBT) filtrate, located at the end of the anaerobic digestion process by maintaining pH between 8.5-8.8 and adding an additional source of magnesium (Mg).

In recent years, multiphase anaerobic digestion systems (Fig. 1) have been introduced to wastewater treatment facilities, with the goal of optimizing acetogenesis in an organic acid (OA) digester to be followed by optimized methanogenesis in a thermophilic digester, with an ultimate purpose of greater methane generation and higher quality biosolids with a lower pathogen load for more widespread distribution.

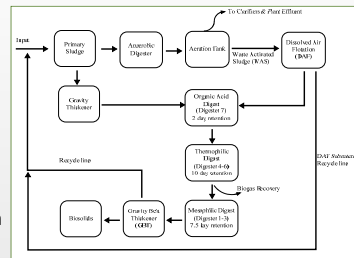


Figure 1. Typical multistage digestion wastewater treatment facility, based on the Madison Metropolitan Sewage District (MMSD) operation

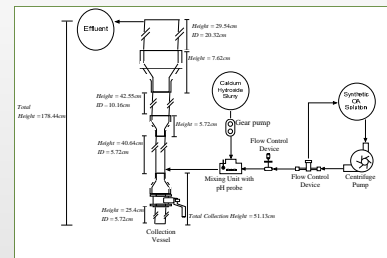
OBJECTIVES

1. Determine the theoretical P recovery potential of the OA digest.
2. Determine how solution pH impacts the recovery and speciation of P minerals produced at the benchtop scale.

MATERIALS & METHODS

The chemical modeling program 'Minteq for Windows v1.5' was utilized to calculate the mineral solubility, and thus the mineral formation potential, for various portions of the multiphase anaerobic digestion process at the Madison Metropolitan Sewage District wastewater treatment plant. Based on this analysis, synthetic organic acid solution was allowed to react in a fluidized bed reactor with calcium hydroxide slurry at various pH values in order to produce calcium phosphates. In a benchtop-scale fluidized bed reactor (Fig. 2) with a hydraulic residence time of 33 min, various rates of $Ca(OH)_2$ were added to the flow of synthetic OA digest solution.

Figure 2. Benchtop Fluidized Bed Reactor used to test synthetic solution (schematic and photo)



RESULTS

At the Madison Metropolitan Sewage District, the OA digest had a significantly greater soluble P concentration, 18.57 mM (572 ppm), than the GBT filtrate, 5.18 mM (161 ppm), and therefore the P recovery potential was greatest for the OA digest. Minteq for Windows predicted that the soluble, reactive P in the OA digest could be recovered as either brushite, a calcium phosphate mineral, through the addition of $Ca(OH)_2$ to pH 6.6 (Fig. 3A), or as struvite, a magnesium phosphate mineral, through the addition of $Mg(OH)_2$ to pH 8.5 (Fig. 3B).

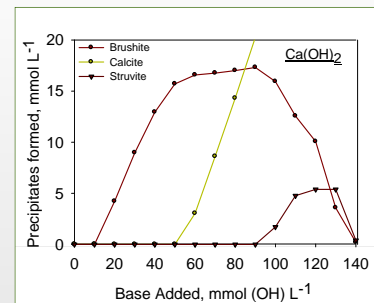


Figure 3A. Predicted mineral precipitation with $Ca(OH)_2$ addition to OA digest.

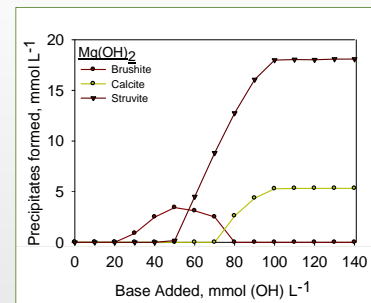


Figure 3B. Predicted mineral precipitation with $Mg(OH)_2$ addition to OA digest.

RESULTS CONT'D

In accordance with chemical modeling, phosphorus precipitation from synthetic OA solution in the fluidized bed reactor increased with pH to 6.5 and ~90% P recovery was achieved (Fig. 4). X-ray diffraction of the solid product showed that brushite was the dominant mineral formed (Fig. 5). Separate batch studies with real OA digest confirm 90% reduction of soluble P as brushite.

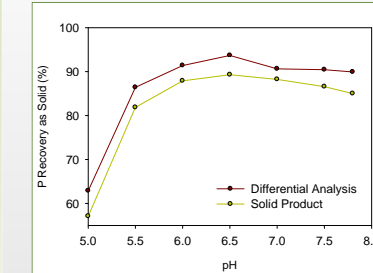


Figure 4. Measured P recovery as a percentage of influent P, based on difference between influent and effluent P concentrations and solid product recovered.

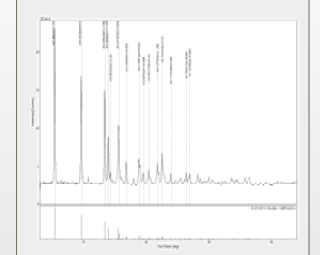


Figure 5. Micrograph (top) of solid product at pH 7.0 and x-ray diffraction pattern compared with brushite, $CaHPO_4 \cdot 2H_2O$ (bottom).

CONCLUSIONS

The purpose of this study was to determine the potential for calcium phosphate recovery from the OA digest and quantify how changes in pH would effect such a system. This study concluded that:

1. The OA digest had three times more soluble, reactive P concentration than GBT filtrate.
2. Chemical modeling predicted this soluble P could be recovered as brushite by adding $Ca(OH)_2$.
3. Brushite formation successfully removed 90% of P in synthetic OA digest solution and could be achieved at a much lower pH, ideally at 6.5, than struvite formation, pH 8.5-8.8.
4. Removal and recovery of P in the OA digester would decrease the incidence of nuisance formation of struvite in the treatment plant and reduce P load in biosolids.

ACKNOWLEDGEMENTS

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