1－10 Phosphorus Recovery from municipal wastewater sludge by adding phosphatase and citric acid as catalyst.

Jitthep Prasityousil*, Yoshimasa Watanabe*, Toshiaki Tadano**
* Department of sanitary and Environmental Engineering,
Faculty of Engineering, Hokkaido University, Sapporo 060,
**Faculty of Agriculture, Hokkaido University, Sapporo 060,

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OBJECTIVE

To study the possibility of phosphorus recovery from municipal wastewater sludge by adding enzyme phosphatase and citric acid as catalyst.

INTRODUCTION

Phosphorus Resources Institute of Japan(1989) estimated that rock phosphate in the world will be remain for 50 to 55 years from 1990. In Japan, the total amount of biological sludge was about 2.2 x 10^6 m^3/year in 1984. There are also a considerable number of water treatment plants that produced chemical sludge of approximately 3 x 10^5 tons(dry basis) per year.

Previous study about phosphorus-forms in sludge (Prasityousil, J et al. 1996), showed that it is possible to recycle phosphorus from excess sludge of wastewater treatment plant by adding enzyme phosphatase and/or citric acid.

Using aluminum-phosphorus complex sludge as fertilizer for agricultural propose, insoluble form of phosphorus has to be changed in form of soluble orthophosphate which plants can be absorb. Insoluble phosphorus can be hydrolyzes but take too much time to recover to be soluble orthophosphate form. The advantage of adding acid phosphatase or citric acid into complex sludge is catalyst hydrolyzing process of phosphorus in complex sludge. Enzyme "acid phosphatase" is used to release PO_4^{-3}-P from organic P compounds. In case of inorganic P compounds, citric acid can be used to recovered soluble form of PO_4^{-3}-P. In natural, plant roots can secrete several organic compounds along with the uptake of water and nutrients. Large amounts of citric acid have been shown to be secreted by *lupin* roots under phosphorus deficient condition, and it has been indicated that citric acid was able to release inorganic phosphorus from phosphatic ferric hydroxide (Gardner et al. 1983). Acid phosphatase is enzyme which can be secreted from plants' roots. This enzyme can release orthophosphate from organically bound

phosphorus.

Watanabe et al(1987) have pointed out many advantages of the combined treatment of chemical and biological sludge. Chemical sludge contains hydroxo-Al or Fe complexes which are capable of absorbing PO_4^{-3}-P through surface coordination reaction. Therefore, adding chemical sludge as coagulant for removing phosphorus from municipal wastewater is possible. From these advantages, it will be more benefit if phosphorus contained in excess sludge can be recycled. Plant can absorb and uptake PO_4^{-3}-P but PO_4^{-3}-P which is found in soil or in excess chemical sludge is insoluble form. Tadano et al(1991) reported that enzyme"acid phosphatase" which is secreted from roots can release PO_4^{-3}-P from organically bound phosphorus to be soluble PO_4^{-3}-P form and secreted citric acid from plant roots can also release PO_4^{-3}-P from inorganically bound phosphorus.

MATERIALS AND METHOD

Wastewater from municipal wastewater treatment plant was used in this study. Sludge from coagulation treatment by various coagulant; $FeCl_3$,$Fe_2(SO_4)_3$ and polyaluminumchloride(PAC) were added enzyme as catalyst for testing the efficiency of phosphorus hydrolysis from sludge. The typical experiment was shown in figure 1. Phosphorus-form in sludge was measured followed by STS method(Schmidt-Thannhauser-Schneider,1945). The properties of acid phosphatase enzyme secreted by roots of *Lupin* are a homo-dimer , molecular weight of the purified enzyme was estimated to be 72 KD by SDS-PAGE and 140 KD by gel filtration, the iso-electric point of the enzyme was 4.7 and the pH for optimum activity was 4.3

RESULTS AND DISCUSSIONS

Figure 2 showed phosphorus-forms in sludge both with and without adding enzyme. In any type of coagulants, organic phosphate compounds in sludge was decreased about 50% when enzyme acid phosphatase was added. In Fe-sludge, protein fraction was decreased more than another organically bound phosphorus. In case of Al-sludge, TNA fraction was decreased more than the another organically bound phosphorus. Furthermore, PO_4^{-3}-P in inorganic phosphate compounds in sludge was also released about 70-80% to be soluble PO_4^{-3}-P which was found in supernatant. All most all of PO_4^{-3}-P in sludge was released to be soluble PO_4^{-3}-P and non-PO_4^{-3}-P (condensed phosphate) fraction was also released to be soluble form. In supernatant, it was quite same percentage of PO_4^{-3}-P fraction that can be absorbed by plants and non-PO_4^{-3}-P fraction which needs citric acid to change these non-fraction to be PO_4^{-3}- P fraction

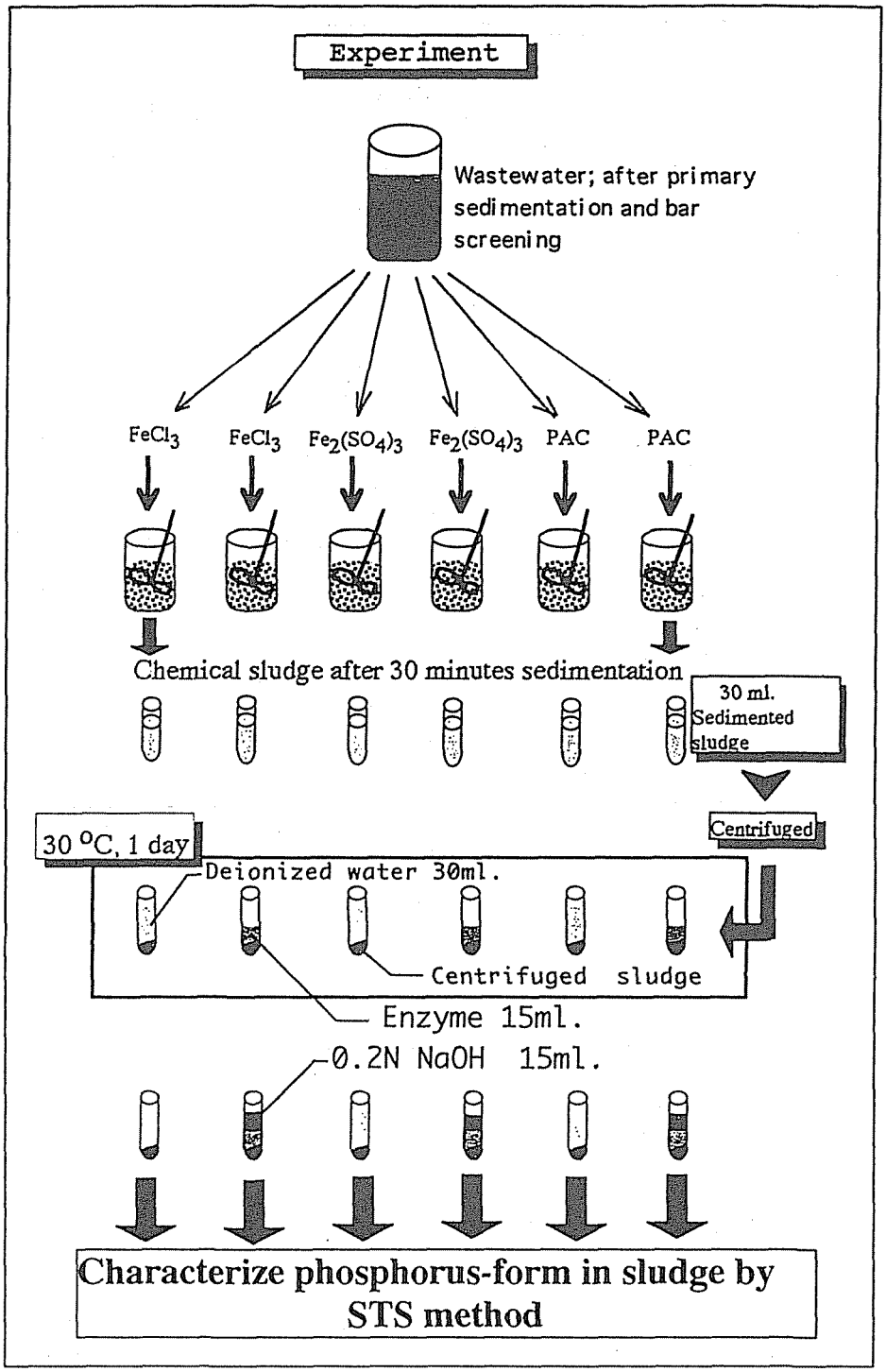

Figure 1 Experiment method

for plants' absorption.

Without adding enzyme in sludge, total phosphorus in supernatant was scarcely found and most phosphorus found in sludge was in form of PO_4^{-3}-P. When added enzyme as catalyst, total phosphorus found in supernatant was about 60-70% recovery and about 50% was PO_4^{-3}- P form and the other form was condensed phosphate. For this phenomenon,

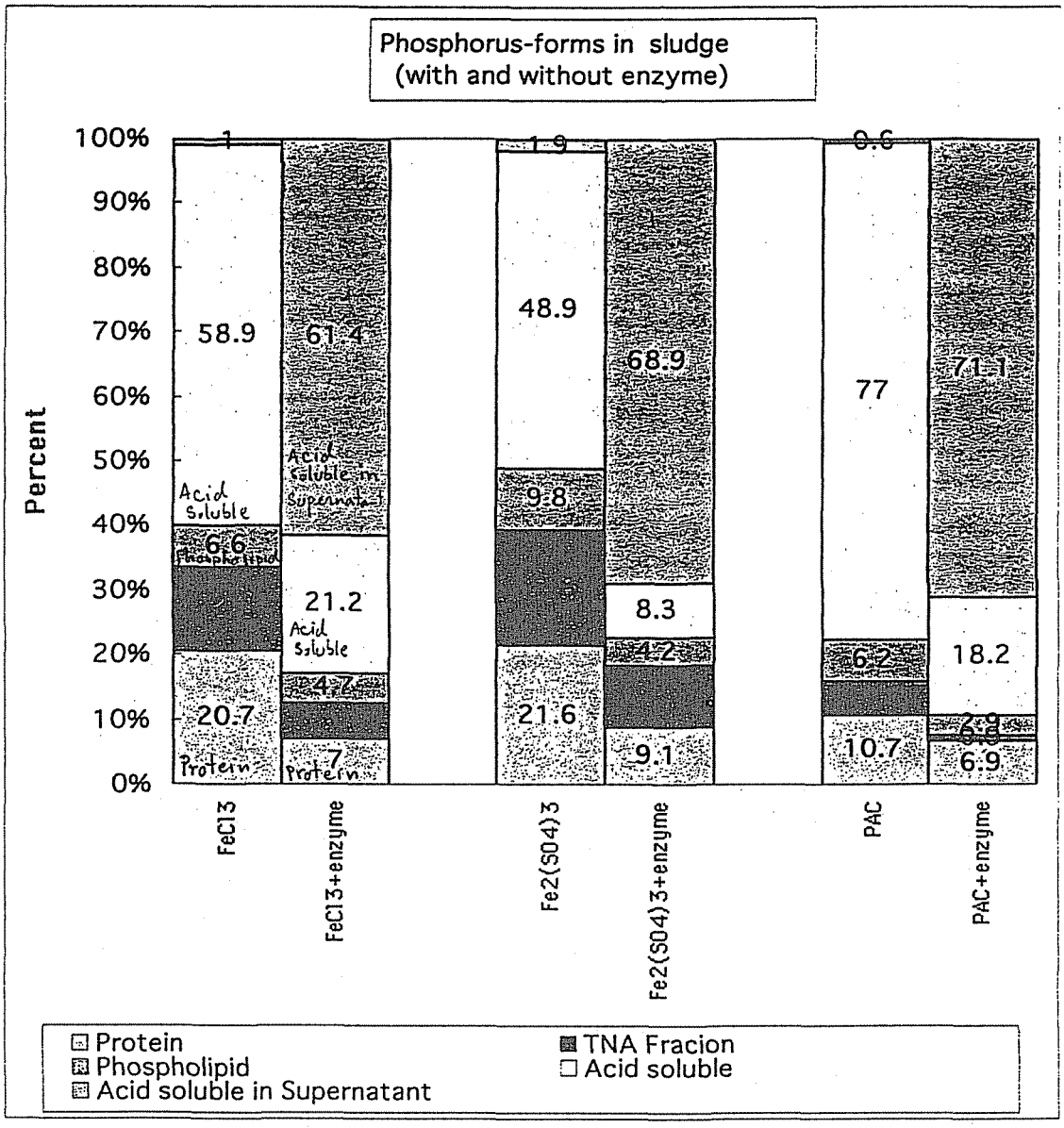

Figure 2 Phosphorus-forms in sludge

assumption are 1) acetate buffer which pH 4.5 could break bond between Al-PO_4^{-3}-P and release free PO_4^{-3}-P. At the same time, enzyme could break bond of Org-P and release free PO_4^{-3}-P. Free PO_4^{-3}-P, then could form bond again with free-Al to be condensed(polyphosphate) form which could be found in supernatant. 2) At the same time that enzyme broke bond of Org-P and released free PO_4^{-3}-P, citrate buffer suddenly made bond of citrate-Al, then there was no free Al ion to form bond with free PO_4^{-3}-P.

This phenomena should be the result from adding buffer solution for control the optimum pH condition for enzyme's reaction. The buffer solution is 0.2 N acetic acid and adjusted to pH 4.5 by 0.2 N sodium

acetate. This buffer solution might react with inorganically bound fraction by some path-way to polyphosphate and then release polyphosphate to orthophosphate. Because it was not only orthophosphate in supernatant but also polyphosphate fraction that could be found. Anyway, adding enzyme in sludge can recovery phosphorus from sludge into acid soluble fraction that plant can absorb.

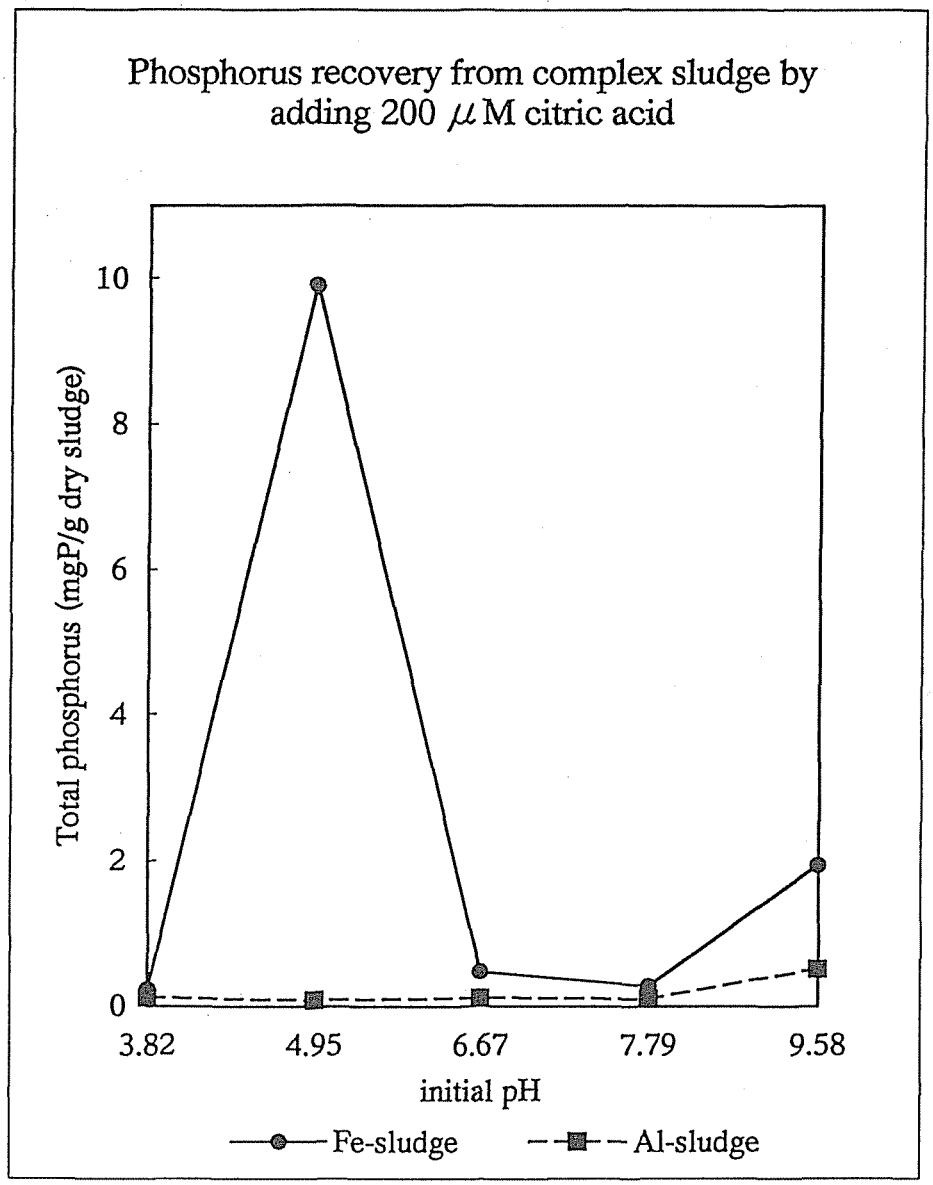

Figure 3 Phosphorus recovery from complex sludge by adding citric acid

Figure 3 showed that citric acid can not catalyst the phosphorus hydrolysis in case of Al-sludge. Phosphorus recovery from Al-sludge per gram of dry sludge was very low compared with phosphorus recovery from Fe-sludge. Total phosphorus concentration in Fe-sludge was about 19 mg.P/g. dry sludge, then from this result, it could be figured out

that 50% of phosphorus recovery could be occurred when adding 200 μM citric acid at optimum pH for citric acid's activity.

Summary

From the results, it is shown that phosphorus recovery from sludge by adding enzyme is one possibility method to recycle phosphorus from wastewater treatment plant for agricultural propose. In case of Al-sludge, acid phosphatase can act as catalyst for releasing PO_4^{-3}-P from organically bound phosphate but citric acid can not act as catalyst for releasing PO_4^{-3}-P from inorganically bound phosphate. For Fe-sludge, it is possible to added enzyme acid phosphatase and citric acid together to catalyst and release PO_4^{-3}-P to be soluble form because the optimum pH for enzyme's activity(pH 4.3) and citric acid's activity(pH 4.95) are similar.

References

1) Prasityousil, J et al. (1996): Characterized Phosphorus-form in excess sludge from hybrid wastewater treatment system. Proc. of the 3rd International Symposium of ETERNET-APR:Conservation of the hydrospheric Environment,II44-II49

2) R.J.L. allen (1640): The Estimation of Phosphorus. J. Biochem, Vol.34,p.858

3) Tanado, T et al. (1991): Secretion of Acid Phosphatase by the roots of Several Crop species under Phosphorus-deficient Conditions. Soil Sci. Plant Nutr.,37(1),129-140

4) Tadano, T et al. (1993): Secretion of Acid Phosphatase by the Roots of Crop Plants under Phosphorus-Deficient Conditions and some Properties of the Enzyme Secreted by Lupin Roots. Plant and Soil155/156: 95-98

5) Watanabe, Y et al. (1988): Reuse of Chemical Sludge for Conditioning of Biological Sludge. Proc. of the 3rd Gothenburg Symposium, 291-306

6) W.C. schneider (1945): Phosphorus Compounds in Animal tissues. I. Extraction and Estimation of desoxypentose Nucleic acid and of Pentose Nucleic Acid. J. Biol Chem., Vol.161,p.193

7) W.C. schneider (1946): Phosphorus Compounds in Animal tissues. III. A Comparision of Methods for the Estimation of Nucleic acid. J. Biol Chem., Vol.164,p.747