

**REMOVAL OF PHOSPHATES IN WASTEWATER
VIA PRECIPITATION: SOME ASPECTS OF
MODIFICATION, CHARACTERISATION AND
OPTIMISATION**

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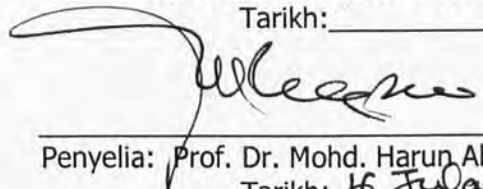
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Puan Dayang, who was always ready to help me in providing materials and apparatus set up in the laboratory.

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ABSTRACT

REMOVAL OF PHOSPHATE IN WASTEWATER VIA PRECIPITATION: SOME ASPECTS OF MODIFICATION, CHARACTERISATION AND OPTIMISATION

Phosphorus and nitrate are major limiting nutrients for algal bloom. When algae decomposes in water systems, biochemical oxygen demand (BOD) would increase and cause other living organisms to be lacking in oxygen. Although phosphate compounds are less used in detergents or other washing agents, it is still widely used in agriculture as a source of fertilizer and its negative effects on the environment are significant. Removal of phosphate and nitrate from wastewaters with conventional ways by using alum, lime and iron will result in producing the precipitated phosphorus and nitrate-bearing salts sludge as waste products that were expensive to handle and transport. However, there is a different approach of removal by precipitating phosphate and nitrate into struvite, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. Struvite can then perhaps be applied as slow fertilizers, raw materials for phosphate industry, also in the making of fire resistant panels and as binding material in cements. Experiments to investigate conditions and parameters that influence the precipitation of struvite are conducted in this research. Molar concentration ratio of 1: 1: 1 with respect to Mg^{2+} , NH_4^+ and PO_4^{3-} stoichiometric concentrations and at pH values of more than 8 were found to have caused an increase in crystal yield. Ratio of Mg^{2+} to the other ions should be at least 1.50 as this ion is an important limiting factor to produce the precipitate. Fe^{2+} ions caused failures in producing struvite as this ion competed with other ions to form iron complexes. Besides all these parameters (molar concentration, pH, excess of Mg^{2+} ions, Fe^{2+} concentration and degree of supersaturation), conditions such as mixing (by stirring the solution with magnetic stirrer) in batch-scale experiments, proved to be indispensable in producing a significant struvite yield. Recycling, in this context means that struvite can be a source of raw material to replace phosphate mining from phosphate rocks and be a renewable nutrient source in the agriculture industry.

ABSTRAK

Fosforus dan nitrat adalah nutrient utama bagi pertumbuhan alga. Apabila alga mengurai dalam sistem air, permintaan biokimia oksigen (BOD) akan meningkat dan menyebabkan hidupan organisma lain kekurangan oksigen. Walaupun sebatian fosfat semakin kurang digunakan dalam detergen atau bahan pencuci lain, namun ia masih digunakan secara meluas dalam bidang pertanian sebagai sumber baja. Maka, kesan ke atas alam sekitar adalah signifikan. Penyingkiran fosfat dan nitrat dari air buangan melalui kaedah lama dengan aluminium sulfat, kalsium hidroksida dan ferum akan menghasilkan lumpur yang dimendakkan oleh garam fosforus dan nitrat sebagai bahan buangan yang mahal untuk dikendali dan diangkut. Walau bagaimanapun, terdapat satu pendekatan penyingkiran yang berbeza iaitu memendakkan fosfat dan nitrat kepada struvit, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. Struvit boleh digunakan sebagai baja, bahan mentah bagi industri fosfat, panel penghadang api dan bahan melekat dalam simen. Eksperimen untuk mengkaji keadaan dan parameter yang mempengaruhi pemendakan struvit dijalankan. Nisbah nilai kepekatan molar 1:1:1 bagi Mg^{2+} , NH_4^+ dan PO_4^{3-} secara stoikiometri dan pada nilai pH yang lebih daripada 8 boleh meningkatkan perolehan hablur. Nisbah Mg^{2+} kepada ion lain perlu bernilai sekurang-kurangnya 1.50 kerana ion Mg^{2+} adalah suatu faktor penghad untuk menghasilkan mendakan. Ion Fe^{2+} menghalang penghasilan struvit kerana ion ini bersaing dengan ion lain untuk membentuk kompleks besi. Selain parameter-parameter tersebut (kepekatan molar, Fe^{2+} dan darjah ketepuan), keadaan seperti pencampuran (kacau larutan dengan pengacau magnet) dalam eksperimen telah dibuktikan sebagai faktor yang mustahak untuk menghasilkan struvit. Kitaran semula dalam konteks ini bermaksud struvit boleh dijadikan bahan mentah untuk menggantikan penggalan fosfat dari batuan fosfat dan sebagai sumber nutrien yang boleh diperbaharui dalam industri pertanian.

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ABBREVIATION

BOD	Biochemical oxygen demand
C_i	Initial concentration
C_f	Final concentration
pH_i	Initial pH value
pH_f	Final pH value
Ps	Conditional solubility product
Pseq	Equilibrium conditional solubility product
Tg	tera gram ($\times 10^{12}$)
Pa	per acre

SYMBOLS

α	Ionization fraction
γ	Activity
μ	Ionic strength
Ω	Degree of supersaturation
\rightleftharpoons	Reversible reaction
$\{ \}$	Effective concentration
Σ	Total / sum
C_{Tri}^{meas}	Total measured concentration of i th ion
C_{Tri}^{theo}	Total theoretical concentration of i th ion
K_{so}	Conditional solubility product

CHAPTER 1

INTRODUCTION

1.1 ROLE AND IMPORTANCE OF PHOSPHORUS IN POLLUTION PHENOMENA

One of the leading water quality issues associated with agriculture in developed countries is nutrient pollution by nitrogen and Phosphorus. Phosphate is only moderately soluble and relative to nitrate, is not very mobile in soils. However, erosion can transport considerable amounts of sediment-adsorbed phosphate to surface waters. If soils have been over-fertilized, rate of dissolved phosphorus losses in runoff will increase due to the build-up of phosphates in soil (Shortle, 2001).

Three elements — carbon, nitrogen and phosphorus — are responsible for nearly all of the pollutant compounds present in domestic or urban wastewaters. Of the three, phosphorus has proven to be particularly recalcitrant. Degradation of carbon-containing pollutants, the largest group, is well understood from a theoretical perspective, and in developed countries, the infrastructure needed for biologically treating this fraction is in place. Biological treatment processes for elimination of nitrogen-containing compounds are well developed, even though the infrastructure is not as complete. Phosphorus treatment, on the other hand, lags relatively far behind; biological removal processes are still in the developmental stage (despite the significant progress that has been made in recent years), and there is almost no infrastructure (limited to a few experimental treatment stations). Given the present state of affairs, chemical processes for phosphorus removal are still of interest for their potential efficiency and reliability, even though they are likely to be more costly than biologically based approaches (Roques, 1996).

The total amount of phosphorus present in municipal wastewaters is typically of the order of 10 to 25 mg/L, 10% of which is decantable. The various sources of these compounds are (per person-equivalent) are shown as below:



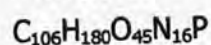
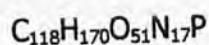
Table 1.1: Amount of phosphorus from various sources (per person-equivalent) (Roques, 1996).

Sources	Per person-equivalent
Metabolic contributions	1.5 g
Water supply	0.1 g
Food preparation and cooking	0.3 g
Detergents	2.1 – 2.3 g
Total	3.9 – 4.2 g

Approximately 50% to 70% of wastewater phosphate compounds are in the orthophosphate form, the balance being polyphosphates and organic phosphorus compounds. For polyphosphates and organic phosphorus compounds, they can be divided into two types of compounds which Leckie and Stumm in Roques, (1996) cite:

- Insoluble or particulate compounds: bacterial and plant debris (phospholipids, phosphoproteins, nucleic acids, phosphate polysaccharides);
- Soluble compounds (glucose- 1-phosphate, ADP, mono- and hexaphosphate inositol, glycerophosphates, phosphocreatine). Polyphosphates and organic phosphorus compounds are hydrolyzed as they pass through a biological treatment plants. The phosphorus present in the clarified effluent is 90% orthophosphate (Roques, 1996).

The heterotrophic biomass responsible for organic matter degradation has relatively limited metabolic phosphorus requirements, and in most cases, the directly assimilable phosphorus already present in the effluent largely exceeds its needs. These requirements can be represented stoichiometrically by simple formulas for microbial biomass, for example:



that is, approximate C to P ratios of 100. The difficulties encountered in biological phosphorus removal [Menar and Jenkins in Roques, (1994), estimate that approximately 2 to 3 mg/L of phosphorus is fixed and eliminated by activated sludge under normal operating conditions] result from this relatively low P requirement. A

means must be found to force the biomass to fix more phosphorus than it needs temporarily (or, even better, permanently) (Roques, 1996).

In a process known as eutrophication, increasing phosphorus and nitrogen levels in slow-moving waters stimulate algae growth and the resulting effects on the aquatic ecology can be dramatic. As algae bloom, they take up dissolved oxygen, depleting the oxygen available for fish and other aquatic life. They can also block sunlight needed by aquatic vegetation, causing the vegetation to die off and loss in vegetation then move up the food chain, leading to the death of fish and other aquatic life (Shortle, 2001).

Waste treatment plant effluents therefore generally contain elevated phosphorus concentrations, largely as orthophosphate, which is then discharged to surface waters. Other less easily evaluated sources of phosphorus pollution include industrial and agricultural wastes, including rainwater dissolution and runoff transport of chemical fertilizers after crop application and animal wastes (either directly or after application as fertilizer). The magnitude of fertilizer and animal waste contributions varies widely, depending on the type of soil involved, vegetation, agricultural practices, etc. Much of the phosphorus will be fixed by the soil (Roques, 1996). For example, estimated amounts for each of these sources for France are given in Table 1.2.

Table 1.2: Sources of phosphorus pollution in France (Roques, 1996).

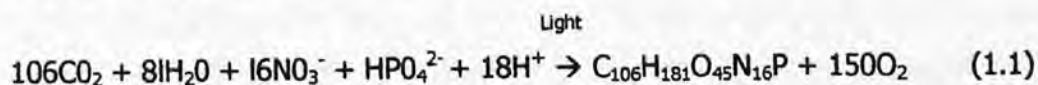
Pollutant sources	Millions of tons of P
Chemical fertilizers	0.86
Animal waste	0.34
Industrial waste	0.004
Municipal waste	0.007

Phosphorus is an essential nutrient of life, contained in protein and ATP. In many lakes and streams, phosphorus is the limiting nutrient for algal and plant growth. An approximate formula for algae or plant matter is $C_{280}H_{560}O_{280}N_{19}P_1$. Algae require from 0.001 to 0.01 mg l⁻¹ phosphorus for growth to take place. Above about 0.5 mg l⁻¹ phosphorus is not a limitation to plant growth and algae, which along with other water plants, will often grow at an alarming rate and completely dominate a

body of water. Consequently, the lower portions of the plant matter will die and while decaying at the bottom of water, will use up most of the oxygen in the water. This process is referred to as eutrophication and results in fish kills and a general degradation of water quality (Greenber *et al.*, 1985).

Eutrophication, the increase in fertility and productivity of an ecosystem due to an increased rate of nutrient input, is perhaps the most pervasive impact of human activities on water bodies system. Eutrophication may be natural, due to the slow increase in fertility of a water body's watershed through geological time. Almost all cases of recent eutrophication, however, are due to human activity. Sewage discharges, organic waste discharges by industries, runoff of fertilizers from agricultural lands, and increased leaching and erosion of watersheds disturbed by farming and construction all increase nutrient inflows to water bodies. For most fresh waters, phosphorus is the limiting nutrient for primary production, and excess inputs of phosphorus the primary culprit in eutrophication due to human activity (Cox, 1997).

A 1970 report of the American Water Works association represented the overall algal growth reaction during the diurnal autotrophic cycle as



Algal growth is accompanied by release of various metabolites. Some of these compounds are responsible for unpleasant tastes and odors, while others are haloform precursor if the water is chlorinated for drinking purposes. In addition, phytoplankton growth can lead to biological oxygen demand (BOD) values which are much higher than the initial BOD in the untreated effluent. During maximum growth periods (summer), the algae release large quantities of oxygen (Equation 1.1) during the day and consume large quantities of oxygen at night when they convert to a heterotrophic metabolism. The resulting nocturnal reduction in dissolved oxygen can lead to large-scale fish kills due to asphyxiation. Increasing temperature and light levels in autumn cause algae to become inactive and sink to bottom, where they are decomposed by anaerobic organisms during winter. Carbon is released as CO_2 and CH_4 , nitrogen and phosphorus components are solubilized, and sulfur is released in the form of H_2S . The acidic CO_2 and H_2S components will dissolve sediment iron and

manganese solids, increasing the amount of Fe and Mn that will need to be removed during subsequent drinking water treatment. These processes do not generally pose a problem for running waters, since algal biomass is limited by continual export to the sea. The quality of stagnant or long-residence-time water bodies can, on the other hand, be significantly degraded, in certain instances compromising any future use for drinking water or industrial purposes (Roques, 1996).

From a mass balance perspective, eutrophication can be considered as a transitory state during which nutrient input either momentarily or permanently exceeds output. The mass balances in these cases must therefore include matter which is exchanged with the gas phase (atmosphere) or eliminated in the form of a solid. Phosphorus occurs in natural waters and in wastewaters almost solely as phosphates. These are classified as orthophosphates, condensed phosphates (pyro-, meta-, and other polyphosphates) and organically bound phosphates. They occur in solution, in particles or detritus, or in the bodies of aquatic organisms (Greenberg *et al.*, 1985).

These forms of phosphate arise from a variety of sources. Small amounts of certain condensed phosphates are added to some water supplies during treatment. Larger quantities of the same compounds may be added when water is used for laundering or other cleaning, because these materials are major constituents of many commercial cleaning preparations. Phosphates are also used extensively in the treatment of boiler waters. Orthophosphates applied to agricultural or residential cultivated land as fertilizers are carried into surface waters with storm runoff and to a lesser extent with melting snow. Organic phosphates are formed primarily by biological processes. They are contributed to sewage by body wastes and food residues and also may be formed from orthophosphates in biological treatment processes or by receiving water biota. Phosphorus is essential to the growth of organisms and can be the nutrient that limits the primary productivity of a body of water. In instances where phosphate is a growth-limiting nutrient, the discharge of raw phosphate or treated wastewater, agricultural drainage, or certain industrial wastes to that water may stimulate the growth of photosynthetic aquatic micro- and macroorganisms in nuisance quantities (Greenberg *et al.*, 1985).

The plankton are composed of plants, phytoplankton are predominantly algae and cyanobacteria, and since they are chlorophyll-bearing organisms, their growth is influenced greatly by the amount of the fertilizing elements nitrogen and phosphorus in the water. Research has shown that nitrogen and phosphorus are both essential for the growth of algae and cyanobacteria and that limitation in amounts of these elements is usually the factor that controls their rate of growth. Experience has shown that such blooms do not occur when nitrogen or phosphorus or both are present in very limited amounts. The critical level for the inorganic phosphorus has been established as somewhere near 0.005 mg/L or 5 µg/L under summer growing conditions (Sawyer *et al.*, 2003).

Domestic wastewater is relatively rich in phosphorus compounds. Prior to the development of synthetic detergents, the content of inorganic phosphorus usually ranged from 2 to 3 mg/L and organic forms varied from 0.5 to 1.0 mg/L. Most of the inorganic phosphorus was contributed by human wastes as a result of the metabolic breakdown of proteins and elimination of the liberated phosphates in the urine. The amount of phosphorus released is a function of protein intake and, for the average person in the United States, this release is considered to be about 1.5 g /day (Sawyer *et al.*, 1994).

Algal blooms occurring near coral reefs can affect corals by preventing the penetration of sunlight, which is essential for the coral growth. Excessive phosphorus also weakens coral skeleton making corals more susceptible to physical damage (Adnan *et al.*, 2003).

1.2 OBJECTIVES

- a. To develop a method to remove phosphorus from wastewater via precipitation of struvite
- b. To investigate the effects of molar ratio, pH, impact of foreign ion (iron), and degree of supersaturation on precipitation of struvite.

c. To evaluate the consequence of excess of Mg^{2+} ion than the others (NH_4^+ and PO_4^{3-}), excess of NH_4^+ than Mg^{2+} and PO_4^{3-} , excess of PO_4^{3-} than Mg^{2+} and NH_4^+ on struvite precipitation.

1.3 STUDY SCOPE

This study of phosphorus removal was conducted at batch-scale in laboratory by using synthetic wastewater as effluent simulation and from the real wastewater. Parameters such as concentration (in molar ratios and degree of supersaturation), impact of foreign ions (iron), pH and excess of Mg^{2+} compared to other ions (NH_4^+ and PO_4^{3-}) were studied. Besides these parameters, condition of the experiments such as mixing or stirring the solution with magnetic stirrer was also run.

1.4 DEFINING THE PROBLEM

Perhaps the most pressing water treatment problem at this time has to do with sludge collected or produced during water treatment. Finding a safe place to put the sludge or a use for it has proved troublesome, and the problem is aggravated by the growing numbers of water treatment systems (Manahan, 1993). The volume of sludge generated with chemical phosphorus precipitation makes up to 49% of the waste volume as shown in Table 1.3 (Adnan *et al.*, 2003).

Table 1.3: Design criteria for 80 to 90% suspended solid removal from raw municipal wastewater by chemical treatment (Liu and Liptak, 2000).

Criteria	Ferric chloride, $FeCl_3$	Alum	Hydrated lime $Ca(OH)_2$
Dose, m/L	80—120	100-150	350—500
Chemical sludge production, kg/mg	159—318	113-226	1814—3175

Improper disposal of wastes continues to be a subject of public and governmental concern. One of the problems to be addressed by legislative action in the U.S. is ocean dumping of sewage sludge. As example, for many years sludge from New York and New Jersey has been disposed in the Atlantic Ocean's 106-Mile

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