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THE PROCESS CONTROLLER's GUIDE TO

PHOSPHORUS REMOVAL FROM WASTEWATER

This is number 4 in the Process Controller Guide series of documents

Number 1	Pollution Control.
Number 2	Water Sources and Water Treatment**.**
Number 3	Wastewater Treatment
Number 4	**Phosphorus Removal from Wastewater.**

It is intended that this document be a useful reference and training manual guide to all persons involved in the Water and Wastewater Industry.

This Process Controller's Guide is a NOT deep investigation into methods of phosphorus removal from wastewater. It is not intended to be used to decide which process of phosphorus removal is indicated for a particular situation.

These documents are dedicated to the thousands of men and women (both present and past) who are involved in the life critical profession of Water and Wastewater Treatment.

July 2020

THE PROCESS CONTROLLER's GUIDE TO

PHOSPHORUS REMOVAL FROM WASTEWATER

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PHOSPHORUS REMOVAL FROM WASTEWATER

PART 1.

BACKGROUND

1.1 INTRODUCTION.

Phosphorus has the chemical symbol – P; Atomic Number of 15 and an Atomic Mass of 31. It is the 13th most common element in the earth's crust and accounts for about 0.1% of the mass of the earth's crust. Phosphorus is a very reactive element and so it is not found in the raw state. It is found mainly as a Calcium Phosphate rock – $Ca_3(PO_4)_2$.

In the Water and Wastewater industry, we will always express the **Phosphorus content as P.** This does not matter if the phosphorus is present as a phosphate ion or combined with organic materials such as phospholipids, polyphosphates etc. In other sciences, such as geology and agriculture, the phosphorus content is often expressed as P_2O_5. This is a very old fashioned way of expressing the phosphorus content

1.2 THE ROLE OF PHOSPHORUS IN HUMANS AND WARM BLOODED ANIMALS.

Phosphorus in the body of humans and other warm blooded animal is major component of bones and of teeth. An average adult human contains about 700 grams of phosphorus of which 85 to 90% in found in the bones and the teeth. Phosphorus is present in the molecules of DNA and RNA. RNA is the compound that "reads" the DNA code to build proteins for the growth, maintenance and repair of cells.

Phosphorus is also a vital component of the cellular processes that use energy. It forms part of the adenosine triphosphate (ATP) – adenosine diphosphate (ADP) energy transfer process. This will be covered in greater detail when the phosphate release and uptake is discussed.

1.3 THE ROLE OF PHOSPHORUS IN PLANTS.

Phosphorus is vital to plant growth and is found in every living plant cell. It is involved in several key plant functions, including energy transfer, photosynthesis, transformation of sugars and starches, nutrient movement within the plant and transfer of genetic characteristics from one generation to the next.

The most important chemical reaction in nature is photosynthesis. Here chlorophyll uses light energy to convert carbon dioxide and water into sugars and releases oxygen. The ATP – ADP reaction mentioned earlier plays an important part in this reaction.

$$\text{Carbon Dioxide + Water} + \boxed{\begin{array}{l}\text{Chlorophyll}\\ \text{Sunlight}\\ \text{Phosphate Energy}\end{array}} \rightarrow \text{Oxygen + Sugars}$$

Phosphorus in the form as phosphates; is usually the growth limiting factor in the growth of plants. Phosphorus in soil is usually present as the phosphate of calcium, magnesium etc. It is only slightly soluble in water and so does not move much in the soil mass.

It is this growth limiting factor that is of concern in water bodies. The growth of aquatic plants including algae has a direct relationship with the phosphate content of the water.

Fertiliser used for agriculture is often in the form of superphosphate of lime, a mixture of calcium dihydrogen phosphate ($Ca(H_2PO_4)_2$), and calcium sulphate dihydrate ($CaSO_4 \cdot 2H_2O$) produced by reacting sulfuric acid and water with calcium phosphate.

1.4 THE ADVERSE EFFECT OF HIGH PHOSPHORUS LEVELS IN WATER BODIES.

High concentrations of algae in water bodies, especially those used for water supply create enormous problems for the treatment of such water. Both free-floating and rooted aquatic weeds can make movement through the water difficult. The covering of large parts of the Hartebeespoort Dam with Water Hyacinth is an example. When aquatic vegetation dies, it sinks to the bottom of the water body and utilises the dissolved oxygen. This can result in fish kills and other problems.

Eutrophication is the process whereby bodies of water, particularly lakes, become enriched with nutrients that alters the numbers and types of organisms present in the water and results in a deterioration in the quality of the water. Water bodies may be categorized in terms of their biological productivity i.e. in terms of the quantity of organic matter formed.

Plants and algae etc depend on nutrients for their growth, if the amount of the important nutrients of Nitrogen and Phosphorus is limited; then they will stop growing. In other words, when they run out of food they cannot grow anymore. Usually phosphorus is the nutrient that is short supply. Therefore if we can limit the quantity of phosphorus in the water body it will limit the growth of plants and algae. That is why Phosphorus is called the growth limiting factor.

If too much phosphorus enters the water body, then the plants and algae will continue to grow and the water body will deteriorate as shown in the various stages below.

1.4.1 The Oligotrophic Lake.

These lakes have low concentration of nutrients. They are often deep and have a large hypolimnion (lower layer) that remains cold. There is dissolved oxygen at all depths through the year. The water would be transparent due to the low algal population. The plankton population would be low.

1.4.2 The Mesotrophic Lake.

These lakes have an increased concentration of nutrients. The presence of a higher concentration of algae would result in the water taking on a greenish tinge. There would be moderate numbers of game fish. There would be some organic matter on the bottom of the lake. In a stratified lake there would be some reduction of the dissolved oxygen content of the water in the hypolimnion.

1.4.3 The Eutrophic Lake.

These lakes have an even higher concentration of nutrients. The water becomes turbid due to the high algal population. In an extreme case the water takes on the appearance of "pea - soup". A deep stratified eutrophic lake will have little or no dissolved oxygen in the hypolimnion. Algal blooms are common, these are seasonal sudden increases in the concentration of algae. The sequence of events is as follows:

1 algae take up and store nitrogen and phosphorus,

2. the algae die and settle to the lake bottom,

3. the dead algae decompose and liberate the nitrogen and phosphorus,

4. the spring overturn carries the nitrogen and phosphorus up to the surface where they promote the growth of new crops of algae and this causes the algal bloom.

1.4.4 The Dystrophic Lake.

These are usually shallow with abudant organic matter in suspension and on the bottom. In stratified dystrophic lakes, dissolved oxygen is generally absent from the hypolimnion. The concentration of calcium, phosphorus and nitrogen are small, but the concentration of humic materials is large. Algal blooms are rare.

In the course of time natural pollution changes oligotrophic lakes sequentially into mesotrophic, eutrophic and finally dystrophic lakes. Man usually hastens this deterioration.

Phosphorus and nitrogen are usually the nutrients that limit the growth of algae, as most water has enough free or combined carbon dioxide to act as a carbon source. The amounts of inorganic nitrogen and phosphorus needed to produce abudant algae growth are relatively small. The generally accepted upper concentration limits for lakes to remain free of algal nuisances is 0.02 mg/l of inorganic phosphorus (i.e. ortho - phosphate). Since certain algae can obtain their nitrogen directly from the atmosphere, inorganic phosphorus is usually taken as being the nutrient that limits the growth of algae, but this is not always so.

1.5 SOURCES OF PHOSPHORUS IN WASTEWATER.

The phosphorus in domestic wastewater comes from two main sources:

1. from the food that we eat and excrete each day. This is about 2 – 3 gram per day as P or 6 – 9 gram per day as PO_4 (phosphate). 1 g of phosphorus (P) is equivalent to 3 g of phosphate (PO_4).

   [Phosphorus has atomic mass of 32 – phosphate has molecular mass of 32 + (4*16) = 96. Therefore 32g P = 96g PO_4].

2. from the use of detergents for clothes washing and dish washing. Here the phosphate compounds are used to prevent the calcium and magnesium in the water from affecting the washing process and also to act as a dispersant to prevent the dirt from settling back on the items being washed.

The typical phosphorus content of wastewater is between 8 and 15 mg/l as P.

1.6 FORMS OF CERTAIN CHEMICALS IN WASTEWATER OF VARYING pH VALUES.

Phosphorus in water is present in different forms depending on the pH of the water or wastewater. To get a better understanding of this, one should first look at the more familiar examples of carbon and of nitrogen.

Later in the sections on biological phosphorus removal, one will be able to see why this is important to understand.

1.6.1 The Various Forms of Carbon in Wastewater.

Carbon in wastewater is present in two main forms:

1. Organic carbon containing compounds such as carbohydrates, fats and proteins;

2. Inorganic carbon in forms of Dissolved Carbon Dioxide, Bicarbonate and Carbonate. This is usually referred to as the Carbonic Species. Which form is present depends on the pH of the liquid as shown in figure 1. What is referred to as Carbonic Acid (H_2CO_3) is mostly carbon dioxide dissolved in water. A small percentage will be present as H^+ and $CO3^{=}$.

   As can be seen in figure 1, which form is the most common depends on the pH value. At a low pH, nearly all is present as Carbon Dioxide dissolved in water (this is shown as H_2CO_3 in figure1. At a high pH value, nearly all is present as the carbonate ion ($CO_3^{=}$). In between pH values, most is present in the bicarbonate ion (HCO_3^{-}).

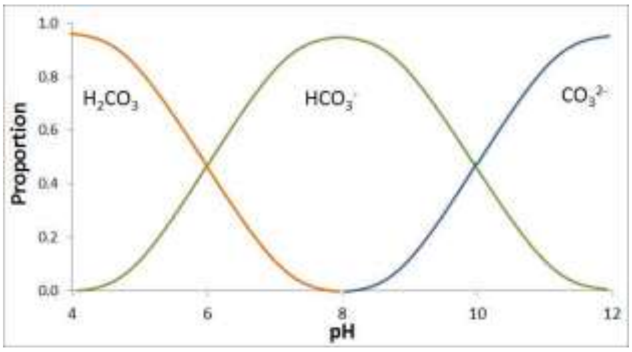

Figure 1 – THE VARIOUS FORMS OF CARBONIC SPECIES AT DIFFERENT pH VALUES.

1.6.2 The Various Forms of Nitrogen in Wastewater.

Nitrogen in wastewater is present in two main forms:

1. Organic compounds such as proteins, amino acids etc;

2. Inorganic nitrogen in forms of the Ammonium Ion (NH_4^+) and as Ammonia dissolved in water. Less than 1 % of the Ammonia dissolved in the water is present as Ammonium Hydroxide (NH_4OH).

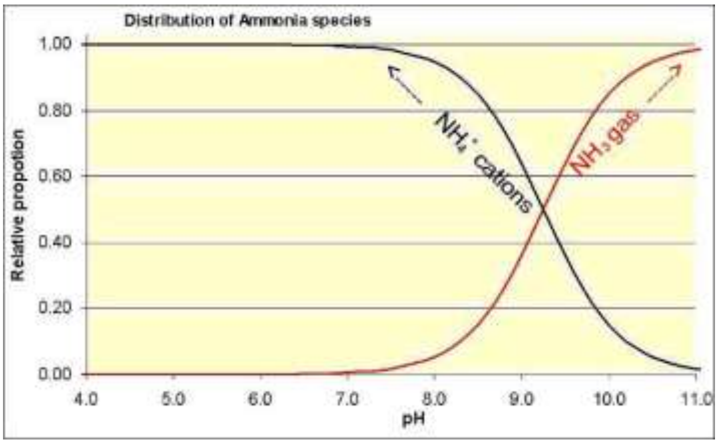

Figure 2 – THE VARIOUS FORMS OF AMMONIA AT DIFFERENT pH VALUES.

1.6.3 The Various Forms of Phosphorus in Wastewater.

Similarly phosphorus may be found in wastewater in two main forms:

1. Organic phosphorus containing compounds such as ATP and ADP (mentioned above), phospholipids (fats containing one or more phosphate groups and phosphoproteins (proteins containing one or more phosphate groups);

2. Inorganic phosphorus containing compounds as shown below:

H_3PO_4	$H_2PO_4^-$	$HPO_4^=$	PO_4^{3-}
Low pH			high pH
Phosphoric Acid	di-Hydrogen phosphate	hydrogen phosphate	ortho phosphate

Which of the above species predominate at various pH values is shown in figure 3.

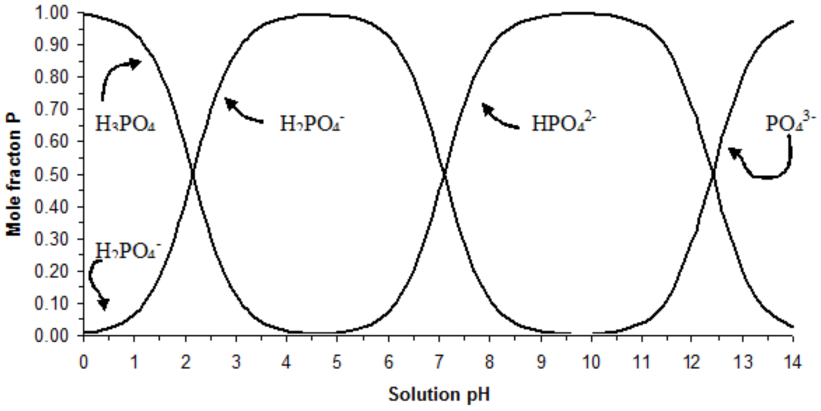

Figure 3 – SHOWING THE PREDOMINANT PHOSPHATE SPECIES AT VARIOUS pH VALUES.

It may be seen at around pH 7 (being close to the value at which wastewater treatment process operate); the di-Hydrogen phosphate and the Hydrogen Phosphate are present in roughly equal amounts.

1.7 PHOSPHORUS IN WASTEWATER TREATMENT.

Phosphorus in wastewater cannot be destroyed. It can be converted from a soluble form into an insoluble form. It can also be removed from the liquid portion of the wastewater and transferred to or incorporated into the solid fraction, namely sludge.

The activated sludge process will generally remove about 5 mg/L of phosphorus in the normal growth of the sludge. This will be removed from the system when the sludge is wasted.

As South Africa is a water scarce country, every effect must be taken to preserve the water supplies that we have. Accordingly, the Department of Water and Sanitation is placing a 1 mg/L limit for Phosphorus in many of the Water Use Licences that they have issued.

PART 2.

REMOVAL OF PHOSPHORUS FROM WASTEWATER BY CHEMICAL METHODS.

2.1 METHODS AVAILABLE TO REMOVE PHOSPHORUS FROM WASTEWATER.

There are two main processes for the removal of phosphorus from wastewater:

1. Chemical;
2. Biological.

Both involve transformation of phosphate in a soluble form to an insoluble form. The latter could be contained in the bio-mass.

2.2 THE CHEMICALS USED TO REMOVE PHOSPHORUS FROM WASTEWATER.

The three most commonly used chemicals used to remove phosphorus from wastewater are:

1. Aluminium based – usually as Aluminium Sulphate $Al_2(SO_4)_3$. 14 H_2O, usually known as Alum;
2. Iron based – usually as Ferric Chloride $FeCl_{3.}$ Less commonly as Ferric Sulphate $Fe_2(SO_4)_3$; Ferrous Chloride $FeCl_2$ or Ferrous Sulphate. – $FeSO_{4;}$
3. Calcium based – lime - $Ca(OH)_2$ can be used but has the major disadvantage that the pH value must be at least 10.0 to get good phosphorus removal. This is outside the normal operating range for a biologically based wastewater treatment works.

2.3 THE CHEMICAL REACTIONS TO REMOVE PHOSPHORUS FROM WASTEWATER.

To simply matters in this Guide, all reactions shown have been on the basis that it is the phosphate ion PO_4 that reacts with the abovementioned chemicals.

1. Using Aluminium Sulphate (also known as Alum).

   This is available as a powder or as a solution. The powder is made of crystals of aluminium sulphate that are combined with 14 molecules of water. The reason why this happens is quite complicated, so it will not be described here. In the powder form, it contains 9.1% of Aluminium.

   Aluminium Sulphate solution contains about 48% aluminium Sulphate by MASS. This means that 1 kg of aluminium sulphate solution contain 0.48 kg of aluminium sulphate or 4.3 g aluminium.

   The Phosphate ion reacts with Aluminium Sulphate as shown below:

   $$Al_2(SO_4)_3.14H_2O \; + \; 2PO_4^{3-} \quad \rightarrow \quad 2AlPO_4 \; + \; 3SO_4^{=} \; + 14\, H_2O$$

   The $AlPO_4$ is insoluble and will accumulate in the sludge.

It can be seen that **ONE atom** of aluminium sulphate reacts with **TWO atoms** of phosphorus (or phosphate).

Remembering that we always express the phosphorus content in mg/l **as P**.

Without going into all the calculations, one can state simply that **9.6 grams of Aluminium Sulphate reacts with 1.0 gram of Phosphorus.**

The above are the THEORETICAL OR STOICHIOMETRIC FIGURES. In actual practice, relatively more aluminium sulphate is required to achieve the desired result. For 90% removal of phosphorus, about **DOUBLE** the above dosage is required.

The main reason why the extra dosage is needed is that aluminium sulphate is acidic. A 1% solution has a pH value of about 3. Being acidic, aluminium sulphate reacts with the carbonic species alkalinity in the wastewater. This may be seen below:

$$Al_2(SO_4)_3.14H_2O + 6HCO_3^{-} \rightarrow 2Al(OH)_3 + 6CO_2 + 14 H_2O + 3SO_4^{=} .$$

The $Al(OH)_3$ is insoluble and will play no further part in the reaction with the phosphate ion, hence the reason to add extra aluminium sulphate.

2. The Reaction with Ferric Salts.

As the Ferric ion has the same charge as aluminium (+3); the reactions are similar to those of aluminium sulphate. The mass ratio of Fe: P is 1.8 : 1. That is **1.8g of Fe reacts with 1.0g of P**. As the Ferric salts are acidic, they will also use up some of the carbonic alkalinity and therefore in practice, higher doses than the theoretical will be required.

3. The Reaction with Lime.

In contrast to the two methods above where an acidic chemical is added to the water, lime has a strongly alkaline reaction. To get satisfactory phosphorus removal, the pH will need to above 9.0. This generally not a problem as the carbon dioxide produced during the oxidation of the carbonaceous material, will neutralise the excess alkali.

2.4 CHEMICAL FEED POINTS.

There are, in theory, 4 possible points where the chemicals may be added. These are:

1. upstream of the primary sedimentation tank;
2. downstream of the primary sedimentation tank, but upstream of the reactor;
3. downstream of the reactor, but upstream of the secondary sedimentation tank;
4. downstream of the secondary sedimentation tank.

These are shown in figure 4 below.

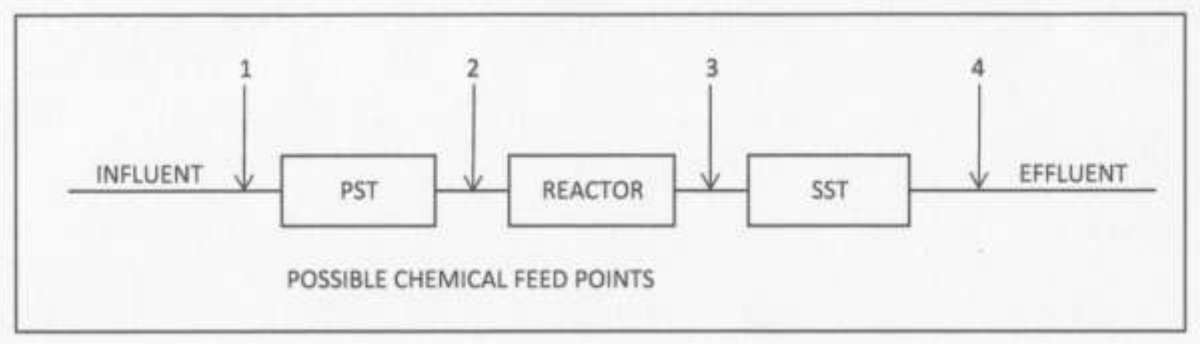

Figure 4 – SHOWING POSSIBLE CHEMICAL DOSING POINTS.

2.4.1 Chemical Addition Upstream of the Primary Sedimentation Tank.

This has a number of advantages as the chemicals being dosed will assist in reducing the suspended solids and the chemical oxygen demand during the primary sedimentation process. This may be seen in table 1 below:

TABLE 1 – TYPICAL REMOVALS ACROSS A PRIMARY SEDIMENTATION TANK WITH AND WITHOUT CHEMICAL DOSING.

PARAMETER	TYPICAL REMOVAL WITHOUT CHEMICAL DOSING	TYPICAL REMOVAL WITH CHEMICAL DOSING
Suspended Solids	40 - 60%	60 - 70%
Biochemical Oxygen Demand	30 - 40%	40 - 50%
Chemical Oxygen Demand	35 – 40%	50% + #
Total Phosphorus	10 – 20%	70 - 90% #

\# - Dose dependent.

An advantage of the improved suspended solids, BOD and COD removals through chemical addition; is the reduction of the organic load on the activated sludge reactor. This would reduce the quantity of waste activated sludge produced and reduce the amount of aeration required.

In water treatment, the coagulation chemicals are added at a point with good mixing to ensure that the coagulant is quickly mixed in the influent before passing into the flocculation zone. Similarly here, the chemical must be dose at a point with good mixing. Thereafter, there needs to be a contact time of about 5 minutes before the flow passes into the primary sedimentation tank.

2.4.2 Chemical Addition Upstream of the Activated Sludge Reactor.

The chemical addition could take place where the inflow discharges into the reactor. However, the improvements in suspended solids, BOD and COD removals shown above; would not take place. On this basis, there would seem to be little advantage in dosing the chemical here.

Of course, in the extended aeration mode for activated sludge (with no primary sedimentation tank); this would be the place or the chemical addition.

The activated sludge process usually removes 2 – 4 mg/L of phosphorus through the sludge production and wasting processes. Chemical addition would improve this. The actual removal would depend on the chemical dosage. The mixed liquor suspended solids would rise and so the sludge wasting would have to be increased.

Without chemical dosing; the ratio between MLVSS (Mixed Liquor **VOLATILE** Suspended Solids) and MLSS (Mixed Liquor Suspended Solids) would remain fairly constant for a particular treatment works. With chemical dosing, the MLVSS would not be affected but the MLSS **WOULD** increase. This change would need to be allowed for when calculating the sludge age when the latter is calculated as:

$$\text{Sludge Age} = \frac{\text{total mass of sludge in reactor}}{\text{mass wasted per day}}$$

2.4.3 Chemical Addition Upstream of the Biological Filter.

Biological filters must have a primary sedimentation stage to prevent blockages in the stone of other medium used. The improved parameter removals as shown in Table 1, would still be applicable.

Although there appears to be no disadvantages of chemical addition at this point, there would also appear to be no advantages either.

2.4.4 Chemical Addition Upstream of the Secondary Sedimentation or Humus Tank.

Having passed through the main secondary treatment process, the biological processes (plus any chemical removal processes) of phosphorus removal are complete. The phosphorus content at this point may still be higher than permitted. Under these conditions, extra chemical addition may be necessary at this point.

It has been found in many instances, that the optimum use of chemicals has been when the chemical dosage is split between upstream of the primary sedimentation tank and upstream of the secondary sedimentation tank. This is shown in figure 5 below:

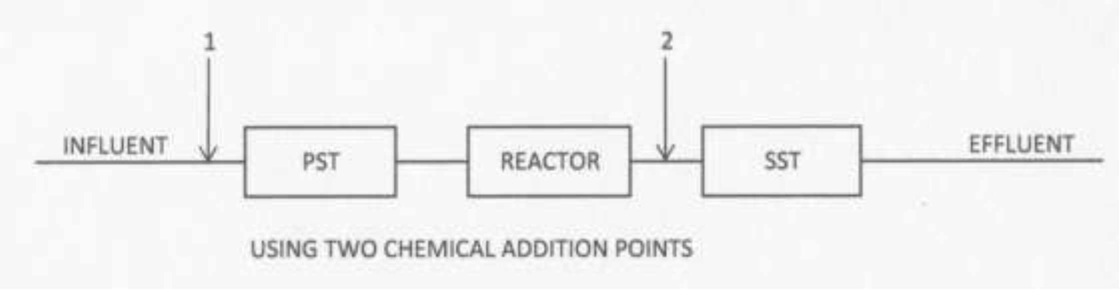

Figure 5 – TYPICAL CHEMICAL ADDITION POINTS FOR OPTIMAL USE OF CHEMICALS.

2.4.5 Chemical Addition Downstream of the Secondary Sedimentation or Humus Tank.

In areas with a very strict limit of phosphorus in the final effluent; it might be necessary to have a final chemical addition point after the secondary treatment process is complete. In this case, it should be regarded as a tertiary treatment process. The chemical addition stage would have to be followed by a sand filtration stage to remove the remaining suspended solids.

A serious disadvantage of this chemical addition point, when using an Iron salt (either in the Ferric form or the Ferrous); is the presence of soluble iron the final effluent.

2.5 OVERALL EFFECT OF CHEMICAL DOSING FOR PHOSPHORUS REMOVAL.

The chemicals used for phosphorus removal when dissolved in water consist of a cation and an anion. The cation is either: Al^{3+}; Fe^{2+}; Fe^{3+} or Ca^{2+}. The anion is either Cl^{-}; $SO_4^{=}$ or OH^{-}. It is only the cation that combines with the phosphate to produce the insoluble compound that is removed from the process. The anion remains is solution and increase the dissolved solids of the wastewater being treated.

This increase in dissolved solids may be seen in the example below:
Assuming a chemical addition of 50 mg/L of Ferric Chloride as Fe.
Atomic mass of Iron is 55.8. Atomic mass of chlorine is 35.5. Therefore molecular mass of Ferric Chloride ($FeCl_3$) is 1x 55.8 + 3x 35.5 = 55.8 + 106.5 = 162.3;

Therefore 50mg/L as Fe = $50 \times \frac{162.3}{58.5}$ = **138.7 mg/l as $FeCl_3$.**

The chloride content of Ferric Chloride = $\frac{3 \times 35.5}{162.3} = \frac{106.5 \times 100}{162.3}$ = **65.6 %.**

Therefore, the chloride added to the water is 65.6 % of 138.7 mg/L = **91 mg/L as Cl.**

As the Total Dissolved Solids of the influent raw wastewater is usually in the range of 600 to 800 mg/L; the increase in dissolved solids by the addition of 50 mg/L of Ferric Chloride expressed as Fe; is significant.

2.6 FURTHER INFORMATION.

Anyone requiring additional information is referred to (amongst others) to:

Process Design Manual for Phosphorus Removal EPA 625/1-76-001a published April 1976 by the Environmental Protection Agency of the United States of America.

PART 3.

REMOVAL OF PHOSPHORUS FROM WASTEWATER BY BIOLOGICAL METHODS.

3.1 INTRODUCTION.

It was seen earlier that the influent phosphorus content of the wastewater is generally between 8 and 15 mg/L. The typical removal through the primary sedimentation stage is 10 to 20%. This means that the concentration of phosphorus entering the secondary treatment stage is usually lies in the range to 6 to 12 mg/L.

The activated sludge process without incorporating any special treatment modifications will remove about 2 – 4 mg/L of phosphorus. By introducing additional stages within the main reactor and manipulating the treatment process; it is possible to obtain significantly higher levels of phosphorus removal by a process known as Enhanced Biological Phosphorus Removal, generally known as EBPR.

This modification is combined with the nitrogen removal process of denitrification as the former is higher dependent on good operation of the latter. Together, the two processes are often known as Biological Nutrient Removal or BNR.

In the sections below; the nitrification / denitrification process is covered first to give an overall understanding of the two processes.

3.2 THE NITRIFICATION and DENITRIFICATION PROCESSES.

As seen earlier in figure 2 that in the range where the nitrifying bacteria are most active (pH 7 – 8); virtually all the ammonia is present as the Ammonium ion (NH_4^+). Nitrification is the oxidation of this Ammonium ion (NH_4^+) -first to Nitrite and secondly to Nitrate. In the first step, the ammonium ion is oxidised to the nitrite ion by the chemo-autotrophic bacteria Nitrosomonas. Chemo-autotrophic means that it gets its energy from the reaction of simple inorganic chemicals. The reaction is:

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2 + 4H^+ + 2H_2O + 2e^-$$

The second step of the nitrification process is the oxidation of nitrite to nitrate by the also chemo-autotrophic Nitrobacter bacteria. The reaction is:

$$2\,NO_2^- + O_2 \rightarrow 2NO_3^-$$

The overall reaction is thus:

$$4NH_4^+ + 4O_2 \rightarrow 2NO_3^- + 4H^+ + 2H_2O + 2e^-$$

Effectively; the ammonium ion is being oxidised to Nitric Acid (HNO_3)

It can be calculated that 1 mg N needs 4.57 mg Oxygen for conversion of the ammonium ion to the nitrate ion. Usually the dissolved oxygen needs to be at about 2 mg/L for complete nitrification.

It is important to note that the overall process produces hydrogen ions (H^+) are produced. These react with the bicarbonate alkalinity to form carbon dioxide as shown below. The alkalinity reduction is 7.14 mg as $CaCO_3$ per mg of ammonia oxidised to nitrate. If the alkalinity of the wastewater is too low then the pH of the mixed liquor may drop and nitrification may be adversely affected and might even cease. The reaction is:

$$H^+ + HCO_3^- \rightarrow CO_2 + H_2O$$

To ensure full nitrification, alkalinity levels (as $CaCO_3$) should be at least eight times the concentration of ammonia (as N) in wastewater. If the amount of alkalinity is less than this, it may be necessary to add lime or soda ash for extra alkalinity.

It would be very useful, if some of the alkalinity that has been lost could be recovered – this happens when denitrification takes place.

The nitrate molecule contains 3 atoms of oxygen for every 1 atom of nitrogen. Again it is would be very useful, if the oxygen tied up in the form of nitrate could be used in the treatment process and so reduce the overall amount of aeration.

It will be seen later in the sections on the biological removal of phosphorus, that the anaerobic zone plays a very important part. IT must be remembered that anaerobic means there must be no nitrates in that zone. Thus a high level of denitrification becomes very important.

The denitrification process achieves all these objectives.

The reduction of nitrate is a multi-step process but the overall process is:

$$2NO_3^- + 10e^- + 12H^+ \rightarrow N_2 + 6H_2O$$

The 10 electrons ($10e^-$) are obtained from the organic material being oxidised by the organisms. It is seen that the hydrogen ions are converted into water; thus reducing the acidity. The above reaction between carbon dioxide and bicarbonate is reversed and so some alkalinity has been recovered. The amount recovered is 2.86 mg as $CaCO_3$ per mg of nitrate reduced to nitrogen gas.

A typical simple nitrification / denitrification activated sludge plant is shown below in figure 6.

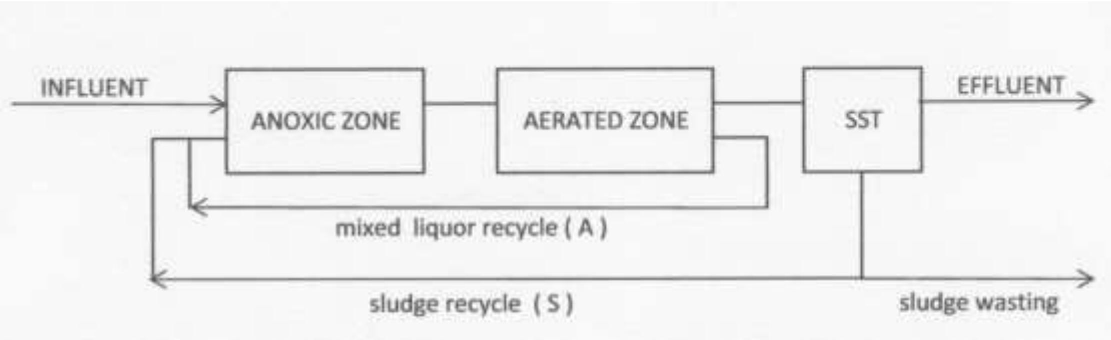

Figure 6 – THE MODIFIED LUDZACK – ETTINGER (MLE) PROCESS FLOW SHEET.

3.3 WHAT IS THE ENHANCED BIOLOGICAL PHOSPHORUS REMOVAL (EBPR) PROCESS?

In one sentence: Certain organisms given the right environment can release phosphorus under certain conditions and later under another condition, take up and store a greater quantity of phosphorus.

The stored phosphorus can range from 5 to 30% on ay-weight basis.

IT was seen earlier, that the activated sludge process, such as the Modified Ludzack – Ettinger process will remove about 5 mg/L of phosphorus. This would still leave a residual phosphorus content of 4 to 8 mg/L. The EBPR can reduce the phosphorus level of the effluent to about 1mg/L as P.

3.4 WHAT ARE THE CONDITIONS FOR EBPR?

There are three zones in the various parts of the activated sludge process where Enhanced Biological Phosphorus removal is required:

1. Oxic – where there is dissolved oxygen present in the liquid. There will also be nitrates present;

2. Anoxic – where there is no dissolved oxygen present, but nitrates are present;

3. Anaerobic – where there is no dissolved oxygen and no nitrates present.

One of the sludge handling processes covered in the ***Process Controller's Guide to wastewater Treatment***; is the anaerobic digestion process. As with the anaerobic process referred to in 3 above; there is no dissolved oxygen present and no nitrates present in the anaerobic digestion process. However, the anaerobic digestion process is more "deeply" anaerobic – that is, it is a more reducing condition whereby even sulphate (SO_4) may be used as a source of oxygen by certain organisms.

This condition would not arise in the activated sludge treatment process.

These three zones are shown below in figure 7:

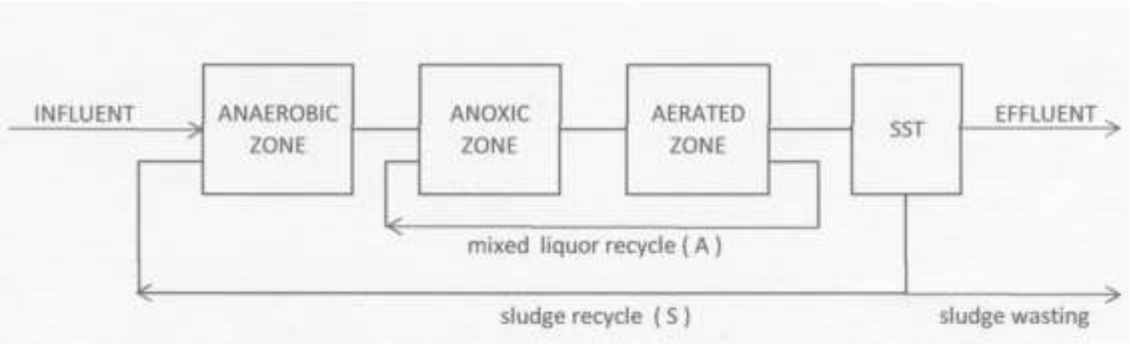

Figure 7 – THE 3 STAGE PHOREDOX PROCESS FLOW SHEET.

3.5 WHAT IS THE ACTUAL PROCESS?

When the influent wastewater enters the anaerobic zone it contains food for the organisms in the form of readily biodegradable organic material. This will contain amongst others short chain fatty acids, known as (SCFA). These include the following.

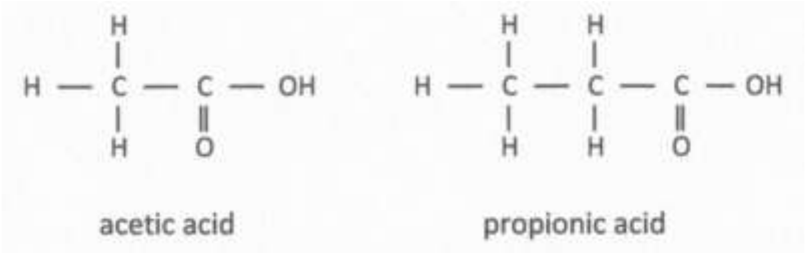

Figure 8 – VOLATILE FATTY ACIDS (2 CARBON and 3 CARBON)

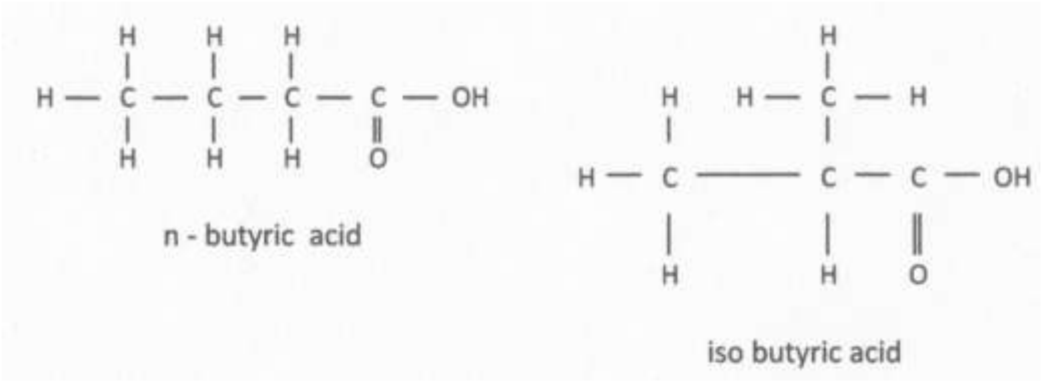

Figure 9 – VOLATILE FATTY ACIDS (4 CARBON).

The organisms that are of greatest interest to us here are the Phosphorus Accumulating Organisms. These are commonly known as PAO’s. These are aerobic organisms in that they grow in the presence of dissolved oxygen in an aerobic environment. They will not grow in an anaerobic environment; they have the unusual ability to consume Volatile Fatty Acids (VFA) under strict anaerobic conditions. Here they store the carbon compounds within their cells.

The energy for this process comes from the hydrolysis of high energy Adenosine Tri phosphate (ATP) into low energy Adenosine Di Phosphate (ADP) and the release of one phosphate group. The nett result of this is an increase in the soluble phosphate content in the anaerobic zone.

In the aerobic phase of the process, PAOs are able to multiply and take up phosphate to replenish the supplies depleted in the anaerobic phase. By oxidizing the carbon reserves built up in the anaerobic phase, PAOs are able to store more phosphate under aerobic conditions than was released under anaerobic conditions because considerably more energy is produced by aerobic oxidation of the stored carbon compounds than was used to store them under anaerobic conditions.

The presence of an adequate source of VFAs is critical to properly condition PAOs in the anaerobic phase of the EBPR cycle. Some Volatile Fatty Acids will be present in the influent to the anaerobic zone. VFAs are also produced though the fermentation of the readily biodegradable carbon material in the anaerobic zone or can be supplemented from other sources. See later regarding the on-site production of volatile fatty acids.

The establishment and maintenance of strictly anaerobic conditions is **CRITICAL** for the PAO’s to consume VFA’s and to store carbon compounds. If any nitrates are present, then the PAO’s are at a competitive disadvantage to other bacterial populations. They MUST accumulate carbon compounds (and release phosphate) during the anaerobic phase or they will NOT take up phosphorus in the aerobic phase.

In the 3 stage Phoredox process shown in figure 5, the “S” recycle from the underflow of the secondary sedimentation tank, is the source of the organisms (and the PAO’s) being returned to the anaerobic zone. This recycle CAN contain nitrates, since the effluent from the reactor will contain some nitrate. It is known that the residence time of the sludge in the secondary sedimentation tank is quite short. There is not much time for any denitrification to take place in the sludge. In fact, denitrification at this stage is not wanted, as it can cause settled sludge to rise and be lost over the effluent weir.

To reduce the nitrate content of the ‘S” recycle, the UCT process was developed Here the “S” recycle is discharged into the anoxic zone where denitrification will take place. A part of the effluent from the anoxic zone is transferred to the anaerobic zone while the rest discharged into the aerated zone. This layout is shown in figure 10.

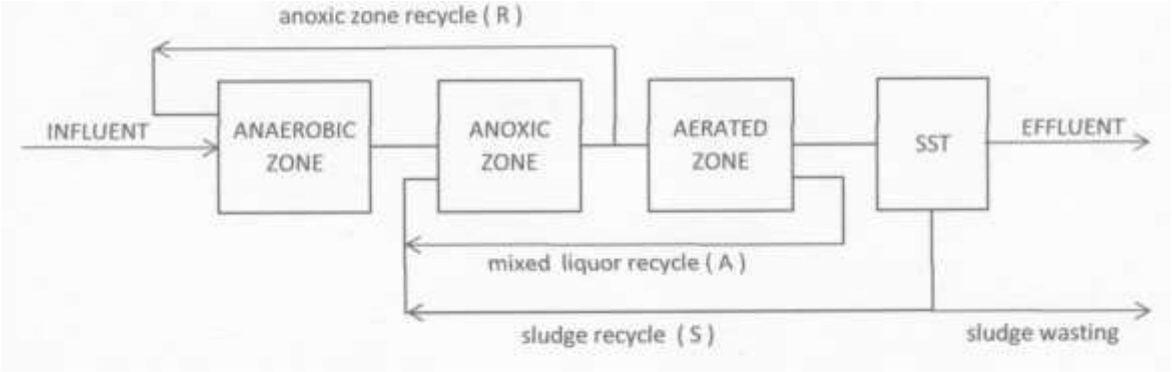

Figure 10 – UCT PROCESS FOR NITROGEN AND PHOSPHORUS REMOVAL.

This layout has been modified to incorporate two anoxic zones to further improve the denitrification of the recycle to the anaerobic zone. This is shown in figure 11 below:

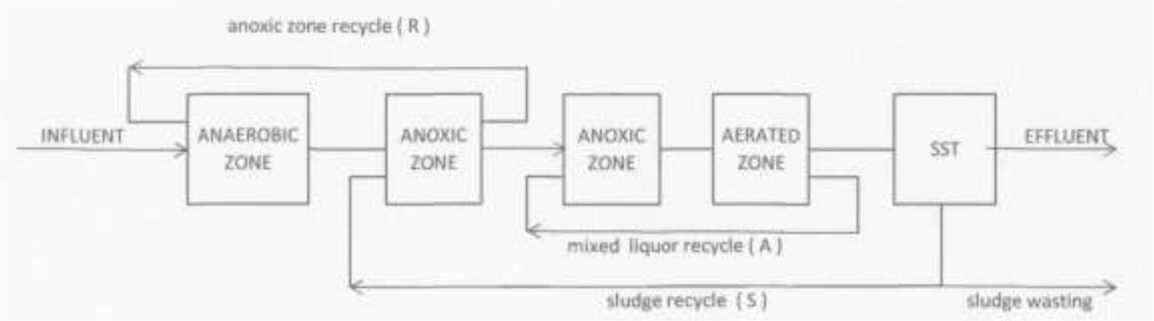

Figure 11 – MODIFIED UCT PROCESS FOR NITROGEN AND PHOSPHORUS REMOVAL.

The UCT process would be fairly easy to retrofit to an existing 3 Stage Phoredox layout. On the other hand, it would be difficult if not impossible to upgrade an existing treatment works to the modified UCT layout. A much simpler layout to incorporate into an existing 3 Stage Phoredox layout, is the JHB (Johannesburg) layout shown in figure 12 below:

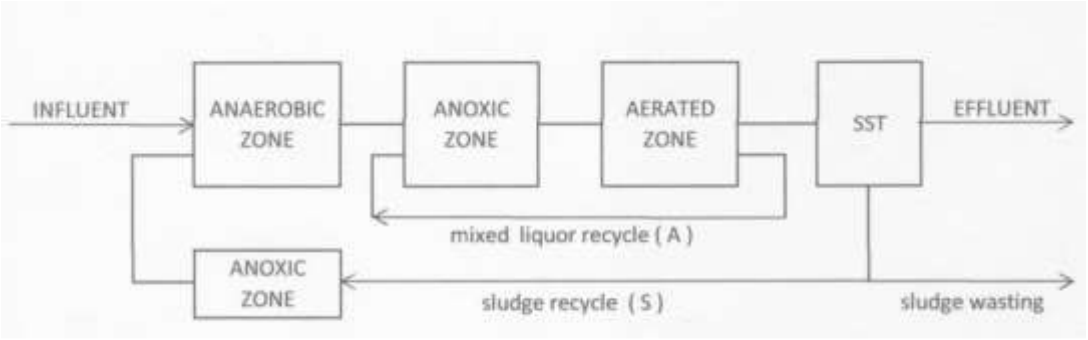

Figure 12 – JHB (JOHANNESBURG) PROCESS FOR PHOSPHORUS REMOVAL.

It may be seen that all three layouts are to try to reduce the nitrate loading on the anaerobic zone to ensure that a strictly anaerobic state is obtained.

At the discharge point from the anaerobic zone, the soluble phosphorus level can be up to 50mg/l as P – compared with an influent phosphorus content of 8 – 15mg/L.
From the anaerobic zone, the wastewater and activated sludge flows into the anoxic zone. Here various organisms use nitrate as an oxygen source to metabolise the carbon containing compounds.

From the anoxic zone, the wastewater and activated sludge pass into the aerated zone. Here the PAO's use the dissolved oxygen to metabolise the Volatile Fatty Acids taken up in the anaerobic zone. They also taken up a large quantity of phosphorus – this is known as "luxury uptake".

3.6 <u>FACTORS AFFECTING THE ENHANCED BIOLOGICAL PHOSPHORUS REMOVAL PROCESS</u>.

3.6.1 It has been noted before that the process can only take place under strictly anaerobic conditions. Hence the various process flow layouts shown above that have been used to achieve the goal;

3.6.2 There must be sufficient Volatile Fatty Acids for the PAO's to take up in order to release as much phosphate as possible in the anaerobic zone. It is possible to produce Volatile Fatty Acids on site by fermentation of primary sludge, allowing it thickener in a thickener and using the supernatant as a source of VFA's;

3.6.3 There is another group of bacteria that complete for the Volatile Fatty Acids. These are the Glycogen Accumulating Organisms. They also release phosphate during the take up of the Volatile Fatty Acids. However, they do not display the "luxury uptake" as performed by the PAO's.

The conditions at which the PAO's can readily out compete the GAO's for the Volatile Fatty Acids, is still the subject of much research. The following factors APPEAR to favour the growth of PAO's over GAO's:

1. higher propionic acid to acetic acid ratio;

2. higher pH in the anaerobic zone;

3. lower COD/P ratio of the order of 10 – 20 mg COD / mg P. Other references suggest a BOD / P ratio of at least 30:1.

From the above, it is clear that more research is required to try to establish what conditions are the most favourable for effective and ongoing stability of Enhanced Biological Phosphorus Removal.

PART 4.

COMPARISON OF THE VARIOUS PHOSPHORUS REMOVAL PROCESSES.

4.1 COMPARISON OF CHEMICAL AND BIOLOGICAL PROCESSES FOR PHOSPHORUS REMOVAL.

POINT OF COMPARISON	CHEMICAL	BIOLOGICAL
Impact on sludge production.	Significant increase in sludge production – up to 40%.	Virtually no increase in sludge production.
Impact on final effluent quality.	Increase in Total Dissolved Solids of effluent; can be significant at higher chemical dosage.	No increase in Total Dissolved Solids.
Impact of influent flow rate variation.	Can be compensated for flow controlled automatic chemical dosing.	Can have adverse effect due to rate of feed to anaerobic zone of VFA's. Especially as internal recycles are usual fixed rate and not influent flow rate adjusted.
Impact of influent strength variation.	Can be compensated for with on-line phosphate analyser linked to automatic chemical dosing.	Can have adverse effect due to rate of feed to anaerobic zone of VFA's.
Operating cost	Much higher due to chemical usage AND higher sludge production for ultimate disposal.	Much lower operating cost.
Capital Cost of construction.	Lower capital cost due to simpler construction.	Much higher capital cost due to extra tanks, pumps and transfer piping.
Ability to retrofit to an existing treatment works/	Relatively easy.	Very difficult and can be almost impossible due to site limitations.
Impact on quality of sludge for beneficial use to land applicable.	Slight impact due to aluminium or iron content, as these are in the insoluble form. Some benefit if calcium used for chemical addition.	Beneficial impact as higher potassium content is associated with higher phosphorus content.
Level of Process Control required.	Moderate. Simplified with on-line phosphorus analyser linked to chemical feed controller.	High level of Process Control required as so many factors influent the effectiveness of the Enhanced Biological Phosphorus Removal process.
Phosphorus content of final effluent that can be attained.	With high enough dose, under 0.1mg/L can be attained.	Lower limit probably about1 mg/L
Overall reliability of the process.	Can be very reliable.	Can be fairly reliable but dependant on so many factors – cannot guarantee always attaining the desired outcome.

4.2 CONCLUSION.

Enhanced Biological Phosphorus Removal can be a very effective process for significantly reducing the phosphorus content of the treated wastewater effluent. If an effluent with a phosphorus content of 1 mg/L or less is required at all times, then a chemical dosing system needs to be installed to complement the process.

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