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NUTRIENT REMOVAL BY MODIFIED ACTIVATED SLUDGE PROCESSES

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ABSTRACT

Stringent wastewater effluent criteria require removal of nutrients from wastewater. Biological processes are now being preferred to chemical precipitation for the removal of nutrients (especially phosphorus) from wastewater, due to a better understanding of the biological nutrient removal mechanisms and reduced operating costs. Modified activated sludge (single-sludge) processes are now being increasingly used for nutrient removal. This article reviews the basic principles and mechanisms involved in nutrient removal from wastewater. Various modified activated sludge processes are studied and compared with an emphasis on design aspects. Nutrient removal capabilities of some treatment plants using various modified activated sludge processes are examined.

INTRODUCTION

The rising demand for water is placing an increased emphasis for effective wastewater treatment and water pollution control strategies. As a result, nutrient removal from wastewater has been a subject of investigation for the last few years [1]. The discharge of effluents laden with nutrients (nitrogen and phosphorus) to natural water bodies creates algal blooms, reduced dissolved oxygen (DO) levels, and thus causes the deterioration of water quality of receiving water bodies. Various biological processes have been developed for the removal of nitrogen,

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phosphorous and their combined removal from wastewater. The mainstream, single-sludge biological phosphorus and nitrogen removal processes for municipal and industrial wastewater treatment are gaining wide acceptance. The main reasons are the reduced capital and operating costs, and reduced sludge production in comparison to other nutrient removal technologies such as chemical and separate stage biological treatment. In this review the basic principles involved in nutrient removal from the municipal wastewater are investigated and modified activated sludge processes for nutrient removal are reviewed with emphasis on design aspects.

BIOLOGICAL NITROGEN REMOVAL

Nitrogen is present in wastewater in various forms. These include organic nitrogen, ammonia, ammonium ions, nitrite, and nitrate [2]. The biological removal of nitrogenous compounds from a municipal wastewater involves the following steps [3]:

1. the use of nitrogen by microbial biomass for cell growth;
2. the conversion of the ammonia and organic nitrogen commonly found in the wastewater to nitrate by autotrophic microorganisms (*Nitrosomonas* and *Nitrobacter*); and
3. the reduction of nitrate to nitrogen gas by denitrifying organisms.

Basic Principles of Nitrification

Nitrification takes place by oxidation of ammonium ion to nitrate with intermediate formation of nitrite. Ammonium ion is converted to nitrite by *Nitrosomonas* as per the following equation:

$$NH_4^+ + 1.5O_2 \rightarrow 2H^+ + H_2O + NO_2^- \tag{1}$$

Nitrite is converted to nitrate by *Nitrobacter* as per the following equation:

$$NO_2^- + 0.5O_2 \rightarrow NO_3^- \tag{2}$$

The overall nitrification reaction included cell synthesis is presented as [4]:

$$1.00NH_4^+ + 1.89O_2 + 0.0805CO_2 \rightarrow 0.0161C_5H_7O_2N + 0.952H_2O + 0.0984NO_3^- + 1.98H^+ \tag{3}$$

From the above equation, it can be deduced that for nitrification of 1 g of NH_4^+-N, 4.6 g of oxygen is required with 1 g of VSS produced and 7.1 g of alkalinity (as $CaCO_3$) destroyed.

It is well established that the rate limiting step for the conversion of ammonium to nitrate is the oxidation of ammonium to nitrite by *Nitrosomonas* [5]. Growth of

Nitrosomonas is limited by concentration of ammonium, while *Nitrobacter* growth is limited by concentration of nitrite. The maximum growth rate of *Nitrobacter* is considerably higher than the maximum growth rate of *Nitrosomonas*, therefore the design of nitrification reactors is controlled by the kinetics of conversion of ammonium to nitrite. The growth of nitrifiers is slow in comparison to the growth of heterotrophic microorganisms responsible for carbonaceous BOD removal [6]. Therefore sufficient solids retention time should be provided to have adequate population of nitrifiers in a treatment system.

The growth rate of nitrifiers can be modeled using the following equation:

$$\mu_N = \hat{\mu}_N \frac{N}{K_N + N} \tag{4}$$

where,

μ_N = specific growth rate of *Nitrosomonas*, d^{-1},
$\hat{\mu}_N$ = maximum specific growth rate of *Nitrosomonas*, d^{-1},
K_N = half-saturation coefficient for *Nitrosomonas*, mg/L
N = NH_4^+-N concentration, mg/L

The maximum specific growth rate of *Nitrosomonas* is dependent upon temperature, DO concentration, pH, feed organic carbon to nitrogen ratio, and the presence of organic and inorganic inhibitors. Nitrification has been shown to occur in the temperature range 4-45°C; the optimum temperature for *Nitrosomonas* growth is 35°C while 35-42°C is optimum for *Nitrobacter* [7, 8]. The variation of $\hat{\mu}_N$ with temperature for the design purposes can be represented by Arrhenius-type expression for temperature range 5-30°C by [4]:

$$\hat{\mu}_N = 0.47e^{0.098(T-15)} \tag{5}$$

T = temperature, °C.

The DO can significantly affect the rate of nitrifier growth and nitrification. Nitrification is reduced for DO concentrations in the range of 0.5-2.5 mg/L, depending upon the degree of mass transport or diffusional resistance and solids retention time for both suspended or attached growth systems [9]. Hanaki et al. observed that low DO (0.5 mg/L) did not affect the ammonium oxidation but inhibits the nitrite oxidation, thus accumulating nitrite in the system [10]. Aeration systems are usually designed for a minimum DO level of 2 mg/L.

Nitrification of 1 g NH_4^+-N destroys 7.1 g alkalinity (as $CaCO_3$) [5]. The equilibrium pH of the reactor is governed by the amount of alkalinity and carbon dioxide present in the system. The nitrification rate can be reduced substantially if the pH is lowered below the neutral range, and for performance stability the optimum pH range is 6.5-8.0 [4]. Nitrification process is also sensitive to the presence of various organic and inorganic inhibitors [11-13].

The ratio of biodegradable organic carbon to nitrogen available for nitrification is a crucial factor affecting the design of nitrification system as the yield of heterotrophic bacteria is much greater than nitrifying bacteria. When mixed liquor suspended solids (MLSS) is the parameter of control, nitrifiers may be washed out from the reactor due to their lower yield coefficient in comparison to hetrotrophs. Thus, the design solids retention time should always be greater than minimum solid retention time for nitrification. An alternative design approach calls for the determination of nitrification rate. But this approach has been shown to be not as effective as the solids retention time approach [4]; it is only useful when site-specific rate is known through pilot-plant studies.

Basic Principles of Denitrification

Denitrification involves the microbial reduction of nitrate to nitrite, and ultimately nitrite to nitrogen gas. Denitrification takes place in the absence of molecular oxygen. In contrast to nitrification, broad range of bacteria can take part in denitrification. Heterotrophic organisms of the genera: *Achromobacter, Acinetobacter, Agrobacterium, Alculigenes, Arthobacter, Bacillus, Chromobacterium, Corynebacterium, Flavobacterium, Hypomicrobium, Moraxella, Neisseria, Paracoccus, Propionibacterium, Pseudomonas, Rhizobium, Rhodopseudomonas, Spirillum*, and *Vibrio* act as denitrifiers [14]. Many of these microbial organisms are present in activated sludge systems, and even in systems not designed for denitrification. In a denitrification process, electrons are transferred from the reduced electron donor usually an organic substrate to an oxidized electron acceptor (nitrate or nitrite). Substrates (as carbon source and electron donors) for denitrification of wastewater include: organics present in the wastewater, methanol, ethanol, acetic acid, and other organic by-products. Mateju et al. reviewed the microbiology, stoichiometry, and different methods of biological denitrification of drinking water [15].

In a denitrification process, reduction of 1 g of nitrate nitrogen is equivalent to the reduction of 2.86 g of oxygen. As mentioned earlier, 4.6 g of oxygen is required to oxidize ammonia nitrogen to nitrate nitrogen and 2.86 g of oxygen equivalents are recovered in denitrification, therefore proper consideration should be given to the reduction of net energy to be expended in providing oxygen in single-sludge activated sludge systems. The electron donors can be provided by the organic substrate or organic compounds added for the completion of the denitrification reaction. The commonly used carbon source is methanol. McCarthy et al. indicated that 2.5 to 3.0 g of methanol was required for denitrification of 1 g of nitrate-nitrogen [16]. The methanol requirement can be calculated using the following equation:

$$M = 2.47(NO_3^-\text{–N}) + 1.53(NO_2^-) + 0.87DO \quad (6)$$

COD requirements for denitrification can be calculated using the following equation [17]:

$$\frac{COD}{N} = \frac{2.86}{1 - 1.134Y_{net}} \tag{7}$$

where,

Y_{NET} = net biomass yield based on COD, g VSS/g COD removed.

The equation was based on the assumption that COD of the VSS produced was 1.42 g COD/g VSS and 10 percent nitrogen was present in the biomass.

The growth rate of denitrifiers is similar to the aerobic heterotrophic microorganisms and greater than nitrifiers. Thus the minimum design solids retention time for nitrogen removal systems will be based on the growth rate of nitrifiers. The rate of denitrification is dependent on the concentrations of nitrate, organic substrate, and dissolved oxygen [5]. The nitrogen removal rates can be related to organism growth using the following equation [4]:

$$q_D = \hat{q}_D \left[\frac{S}{K_s + S}\right]\left[\frac{D}{K_D + D}\right]\left[\frac{K_o}{K_o + S_o}\right] \tag{8}$$

where,

S = concentration of organic substrate, mg/L
D = concentration of nitrate nitrogen, mg/L
S_O = DO concentration, mg/L
K_S, K_D, and K_O = half-saturation coefficient, mg/L.

The values of K_D can range from 0.08 to 0.2 mg NO_3/L [18]. Values of K_s reported in literature range from 0.1 to 72 mg/L [4, 19]. For K_o a value of 0.1 mg/L has been suggested [4]. The temperature dependency of denitrification rate can be expressed by:

$$q_{D,T} = q_{20}\theta^{(T-20)} \tag{9}$$

The value of θ has been found to be 1.09 [20] and 1.08 without addition of any organic substrate and 1.07 with methanol, acetone, and acetic acid as substrates [21]. Denitrification is sensitive to pH and optimum pH values lie in the range of 6-8. The denitrifiers are less sensitive to inhibitory organic and inorganic compounds as compared to nitrifiers.

The rate of nitrate removal can also be computed from the rate of substrate removal using expressions used to relate oxygen consumption to organic substrate utilization. For designing denitrification zones after the aerobic zone, the denitrification rate is dependent on the respiration rate of the microorganisms using the stored food reservoirs or substrates released from endogenous decay. The specific denitrification rate ranges from 0.015 to 0.06 g/g-d. If methanol is used as a carbon

source, higher specific denitrification rates ranging from 0.1 to 1.2 g NO_3^--N/g TSS-d have been observed [22].

BIOLOGICAL NITROGEN REMOVAL SYSTEMS

In this section, various treatment options are discussed, compared and their suitability is evaluated. The three approaches that can be adopted for nitrogen removal are as follows [3]:

1. separate stages for carbon oxidation, nitrification, and denitrification;
2. combined carbon oxidation and nitrification and separate stage for denitrification; and
3. combined carbon oxidation, nitrification, and denitrification.

The processes in which carbon oxidation and nitrification take place in the same reactor are termed as single sludge systems and are the focus of this review.

Wuhrmann Process

Wuhrmann process was one of the first documented single-sludge nitrification-denitrification processes for municipal wastewater [23]. The process flow diagram is shown in Figure 1. The wastewater enters the aerobic zone where carbon oxidation and nitrification takes place. The wastewater then enters the denitrification zone where endogenous decay provides energy for denitrification. The Wuhrmann process has been found to be unsuitable for full scale plants due to high suspended solids and ammonia levels resulting from the presence of dead cells in the effluent and low denitrification rates.

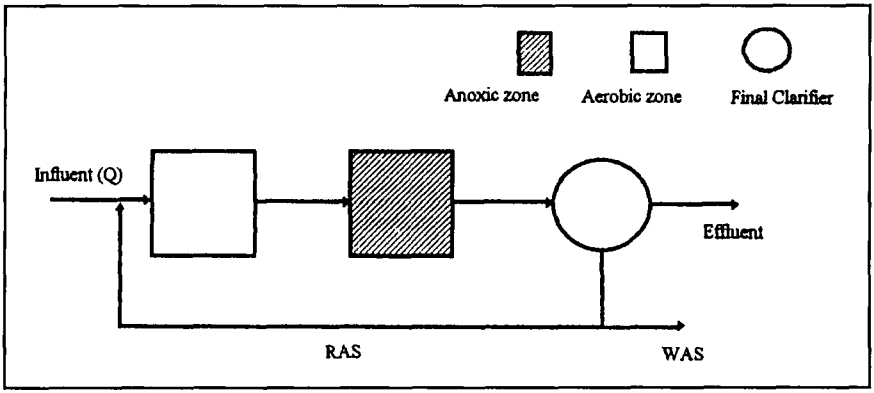

Figure 1. Wuhrmann process [4].

Ludzack-Ettinger Process

In Ludzack-Ettinger process the anoxic zone is placed before the aerobic zone [24] (Figure 2). The denitrification process uses the exogenous carbon provided by the wastewater. The return activated sludge to anoxic reactor ranges from 20 to 100 percent of influent flow rate. The process described above does not provide enough nitrates for heterotrophic denitrification population.

Modified Ludzack-Ettinger Process

Ludzack-Ettinger process was modified by returning the MLSS from the aerobic zone to anoxic zone [25] (Figure 3). The modification resulted in a higher removal efficiency (up to 80%) for total nitrogen. The modified Ludzack-Ettinger process served as the basis for the development of A^2/O, Five stage Bardenpho, UCT, and VIP processes. These processes are capable of both phosphorous and nitrogen removal and will be discussed in detail subsequently.

The processes using single anoxic zones are not effective in producing total nitrogen concentrations < 8 mg/L, without methanol supplement. A total nitrogen effluent concentration of < 6 mg/L can be achieved without the addition of methanol by placing an endogenous anoxic zone in series after the aerobic zone. Such a process is often referred to as the double anoxic zone process.

Four Stage Bardenpho Process

Four stage Bardenpho process uses both wastewater carbon and endogenous decay of carbon for denitrification (Figure 4). The wastewater enters an anoxic reactor which also receives the mixed liquor from combined carbon oxidation/ nitrification zone. The carbon in the influent wastewater is used for denitrification.

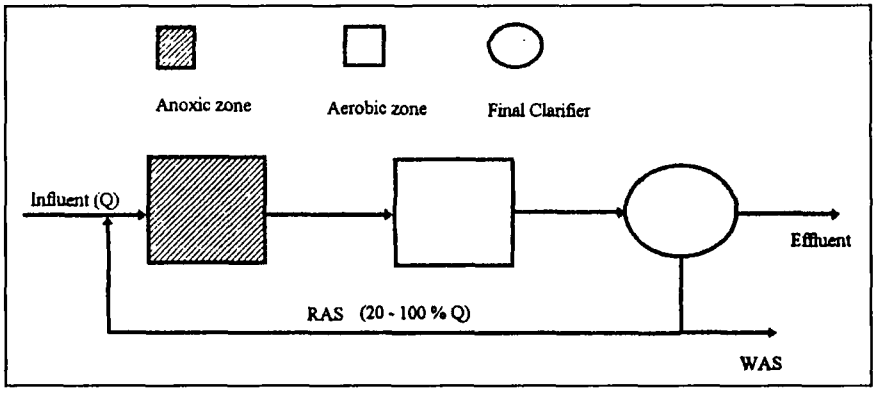

Figure 2. Ludzack and Ettinger process [3].

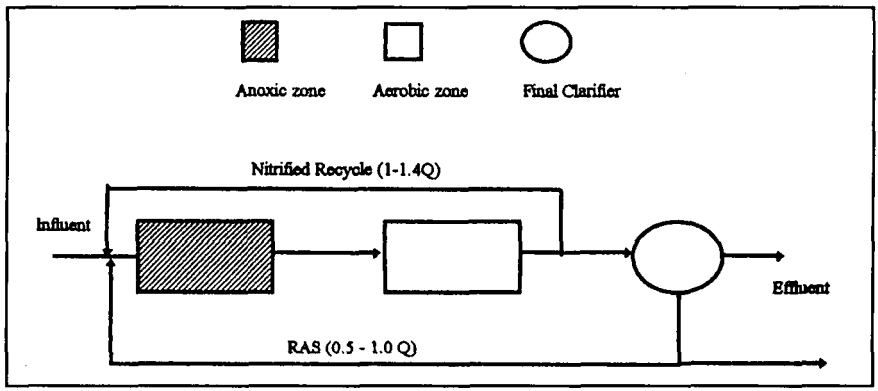

Figure 3. Modified Ludzack-Ettinger process [4].

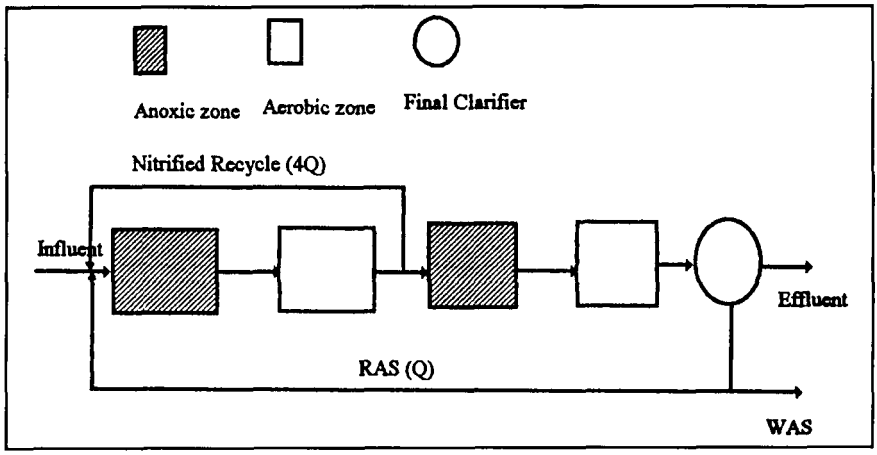

Figure 4. Four stage Bardenpho process [40].

The ammonia in the influent is converted to nitrate in the first aerobic zone. In the second anoxic zone additional denitrification occurs using endogenous carbon source. The second aeration zone is provided after the final anoxic zone to release nitrogen gas and improve the sludge settleability. Use of an external carbon source for denitrification not only adds to the operating costs but also results in increased (10 to 20%) sludge production [26].

The design procedures for single sludge, single anoxic, and double anoxic nitrification-denitrification systems consist of sizing the aerobic zone to nitrify the influent total Kjeldahl nitrogen (TKN) and then sizing the first anoxic zone.

The first anoxic zone should be sized to completely denitrify the internal and RAS recycled nitrates. The second anoxic basin will have higher volume per mass of nitrates applied as endogenous denitrification rates are much slower than those of exogenous rates. Table 1 shows the design criteria for nitrogen removal systems [4].

Typical effluent nitrogen concentrations from activated sludge nitrification-denitrification plants ranged from 6 to 10 mg/L [26]. The nitrogen in effluent was believed to be composed of five fractions. These fractions, their concentrations, and the possible reasons for higher concentrations in the effluents are presented in Table 2. Burns et al. tested modified Ludzack and Ettinger process and Four stage Bardenpho process for their nutrient removal capabilities [27]. Both the processes reduced the TKN by 90 percent (to approximately 2 mg/L) and total nitrogen (TN) by 60 to 75 percent and total phosphorus (TP) by 85 percent (the effluent concentration of 0.4 mg/L).

BIOLOGICAL PHOSPHORUS REMOVAL

Basic Concepts

Phosphorus is present in wastewater as orthophosphate (PO_4^{3-}), polyphosphate (P_2O_7) and organically bound phosphorus; the last two components accounting for up to 70 percent of the influent phosphorus [2]. The potential of biological systems for phosphorous removal is well documented and reviewed [28-30].

Greenberg et al. indicated that activated sludge process can take up phosphorus in excessive amounts [31]. Srinath et al. also reported excessive phosphorus

Table 1. Typical Design Criteria for Nitrogen Removal Systems [4].

Parameter	Single Anoxic Zone Process	Four Stage Bardenpho Process
MLSS, mg/L	1500-4000	2000-5000
HRT, hr		
First anoxic	0.5-2	2-5
Aerobic	2.5-6	4-12
Second anoxic	—	2-5
Reaeration	—	0.5-1
θ_c, d	5-10	10-40
RAS, %	50-100	100
Internal cycle, %	100-400	400-600
F/M, g BOD_5 / (g MLVSS) / d	0.1-0.3	0.1-0.2

Table 2. Typical Effluent Concentrations of Various Nitrogen Fractions Present in Wastewater [26]

Nitrogen Compounds	Typical Effluent Concentrations, mg/L	Reasons for High Effluent Concentrations
Suspended organic	1-2	Bulking and rising of sludge
Soluble organic	1-2	Influent and industry
Nitrate	2-4	Poor denitrification or overloading
Nitrite	0-0.1	Poor process control or nitrogen shock loads
Ammonia	0.2	Lower sludge age for nitrification or nitrogen shock loads

uptake by activated sludge in comparison to the normal metabolic requirements [32]. Levin and Shapiro observed an enhanced biological phosphorus removal (up to 80%) in activated sludge plant and proposed the term "luxury uptake" of phosphorus based on their observations [33]. A biochemical model for biological phosphorus removal was proposed based on the results of Nicholls and Osborn, and Marais et al. [34, 35].

Under anaerobic conditions (absence of oxygen and nitrates as terminal acceptors), simple substrates, such as short chain fatty acids, are transported across the membrane and are stored as insoluble lipid poly-β-hydroxybutyrate (PHB) and poly-β-hydroxyvalarate (PHV), and this was linked to the phosphorus release. The PHB and PHV are then degraded under aerobic conditions to produce energy required for polyphosphate removal. Enhanced phosphorus removal in biological nutrient removal treatment plants to a certain extent also takes place due to chemical precipitation of phosphorus. The phosphate precipitation has been proposed to be mediated by anaerobic phosphorus release and precipitation in biofilms mediated by denitrification (an alkalinity producing reaction) [28].

Study on sludges from Baltimore Back River and Seneca Fall plants identified *Acinetobacter* to be associated with phosphorus removal [36]. *Pseudomonas* and *Aeromonas* are also commonly present in biological phosphorus removal systems [37]. Various steps involved in the biological phosphorus removal systems are summarized in Figure 5 [37].

Biological Phosphorus Removal Processes

Phosphorus removal during secondary biological treatment by sludge wasting ranges from 10 to 30 percent for a phosphorus content of 1.5 to 3 percent in microbial solids. By using the specific biological systems designed for

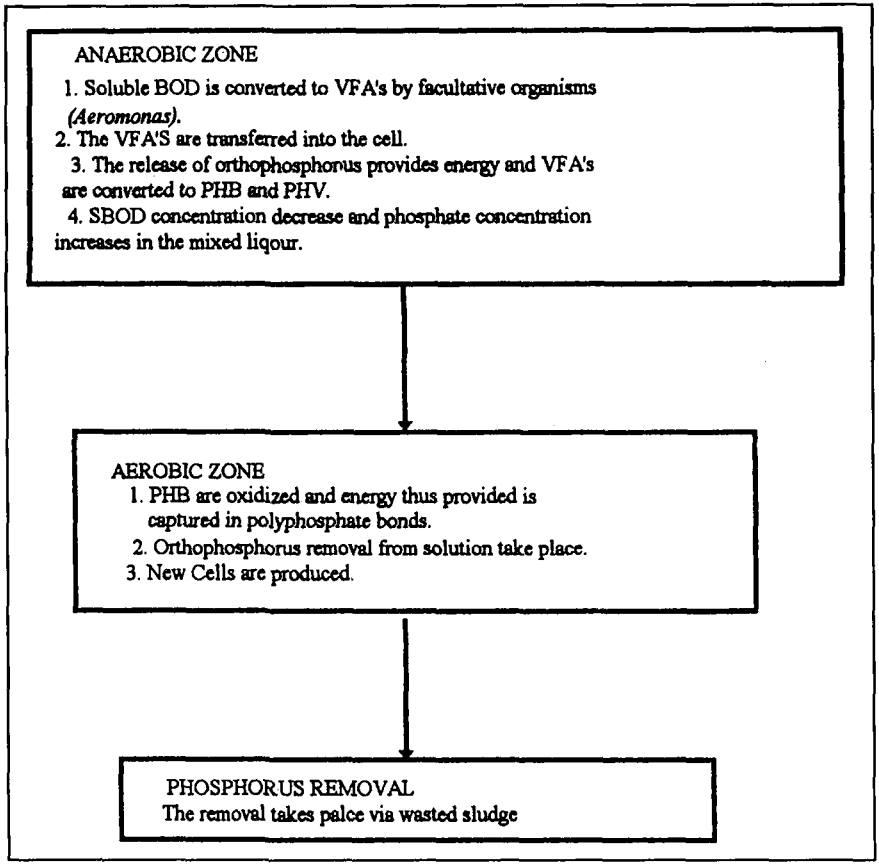

Figure 5. Biological phosphorus removal [37].

phosphorus removal, significantly high removals are achieved. The phosphorus content of waste sludges has been found to range from 2 to 7.3 percent on a dry weight basis [38]. The wastage of biomass solids results in approximately 2.5 to 4 times more phosphorus removal than conventional activated sludge systems. In recent years, a number of biological phosphorus removal processes have been developed.

Mainstream and Sidestream Processes of Biological P-Removal

In mainstream processes phosphorus is concentrated in the activated sludge by passing wastewater through anaerobic and aerobic zone. This P-rich sludge needs aerobic sludge treatment, otherwise phosphorus would be released and

discharged to the influent of the treatment plant. Some of the systems of biological P-removal in the mainstream are A/O, A^2/O, UCT, BB, Phoredox, Biodenipho, and modified oxidation ditch and Carrousel processes.

Biological P-removal in the sidestream (Figure 6) is characterized by keeping the phosphate-rich sludge under anaerobic conditions in a stripper tank in a sidestream of a wastewater treatment plant, with or without a dosage of substrate. The phosphate can hence be released in a controlled way. The stripped sludge is sent back to the aeration basin for P-uptake, while the enriched supernatant can be treated by one of the physicochemical processes, e.g., chemical precipitation, fluid-bed pellet reactor or magnetic separation. In addition to P-removal, the stripper tank also serves as a means for the selection of facultative anaerobic organisms, which produce low fatty acids for *Acinetobacter*. Examples of the systems in the sidestream are the PhoStrip and POH process.

PhoStrip

The PhoStrip process comprises of an aerobic zone, and a secondary clarifier tank [39]. The sludge from the secondary clarifier passes through a stripping tank

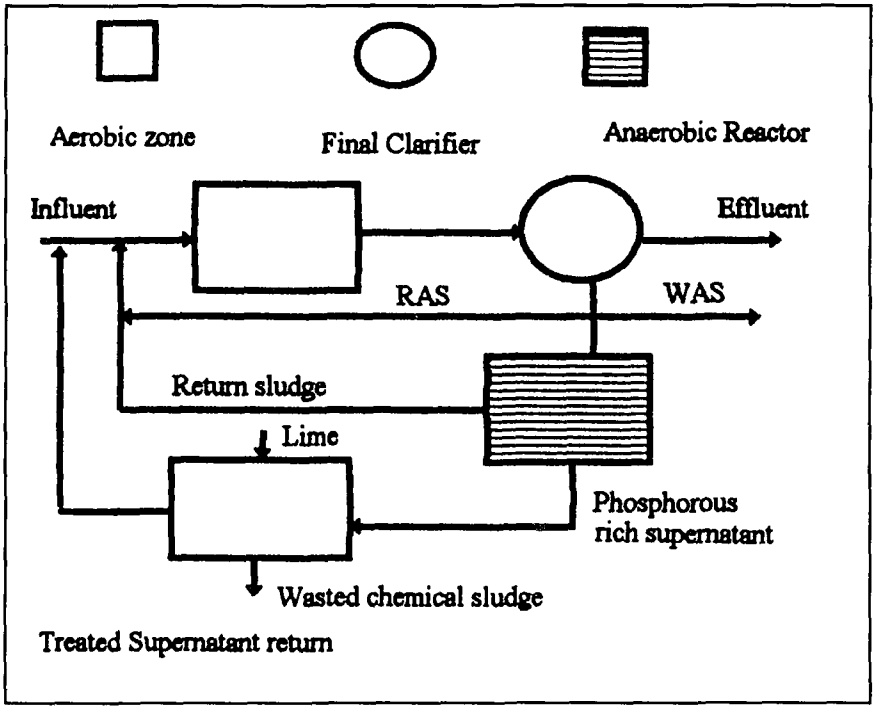

Figure 6. The PhoStrip process [38].

where sludge is exposed to anaerobic conditions for eight to twelve hours. The phosphorous is released from the sludge during this exposure. The soluble phosphorous is then precipitated using lime. The lime dosage also depends on the alkalinity of the wastewater. Figure 6 shows the PhoStrip process.

Phoredox

The Bardenpho process for denitrification was modified to develop Phoredox process for high phosphorus removals [40, 41]. In this process the return activated sludge (RAS) is mixed with the influent wastewater in an anaerobic zone for phosphorus release. In case nitrification occurs, the nitrates in RAS sludge will prevent the anaerobic conditions, thus affecting the phosphorus release. To overcome this difficulty an anoxic zone is provided where denitrification will result in reduced nitrate levels in RAS. Figure 7 shows a schematic of the Phoredox process.

A/O Process

The A/O process is a proprietary process developed by Air Products and Chemical, Inc. and is now marketed by I. Kruger, Inc. [42]. The process consists of anaerobic and aerobic basins (Figure 8). The anaerobic and aerobic zones are divided into a number of equal size complete mix compartments. Usually four and

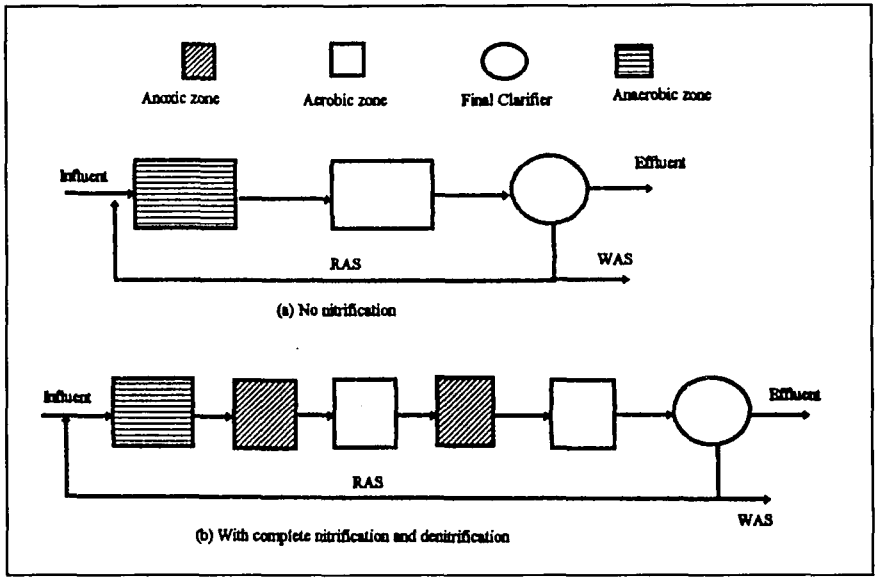

Figure 7. The Phoredox process [40].

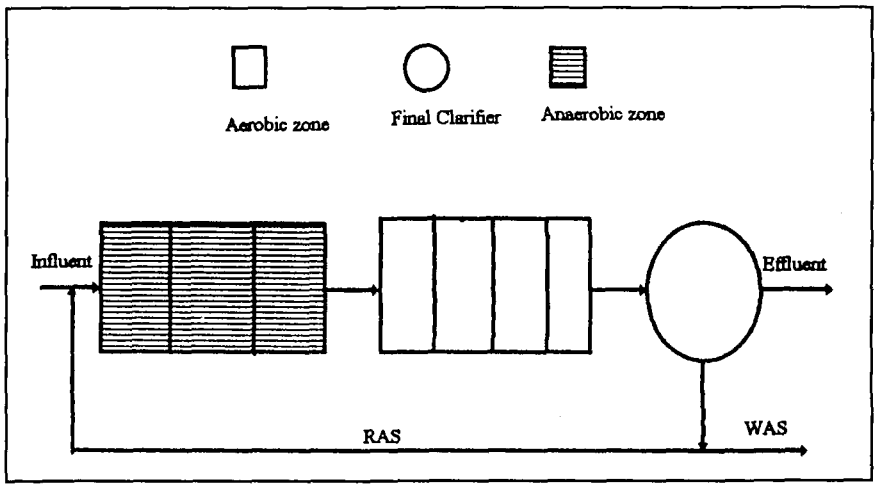

Figure 8. The A/O process [38].

three compartments are provided for aerobic and anaerobic zones respectively. The RAS and the influent pass through an anaerobic zone and then to an aerobic zone. The process operates on relatively short solids retention time, and exhibits an increased sludge production and phosphorous removal rates.

The Rotanox process is similar to A/O process (Figure 9) but there is no separate anaerobic zone and the anoxic and aerobic sections are combined, working on the principle of rotary flow through an anoxic zone [30, 43].

Activated Primary Process

In the activated primary process the VFA's generated by fermentation in a primary clarifier and thickener are fed to the anaerobic zone to facilitate the phosphorus release [41] (Figure 10). This helps in achieving higher phosphorus removal if the influent wastewater falls short of easily degradable COD. The production of acetates and mixing with the influent reduces the detention time to about one hour in the anaerobic zone. This has also shown to reduce the secondary phosphate release. The Bardenpho process in Kelowna, B.C., Canada recycles the acetate produced in the thickener to the influent for high phosphorus removal [44].

Table 3 shows a summary of typical recommended design criteria for the PhoStrip and A/O [2, 4]. A significant design feature to be noted among these processes is the operating organic loading. The PhoStrip process is not restricted to the limited range of organic loading in comparison to the A/O process. The A/O process is generally designed as a high rate activated sludge system.

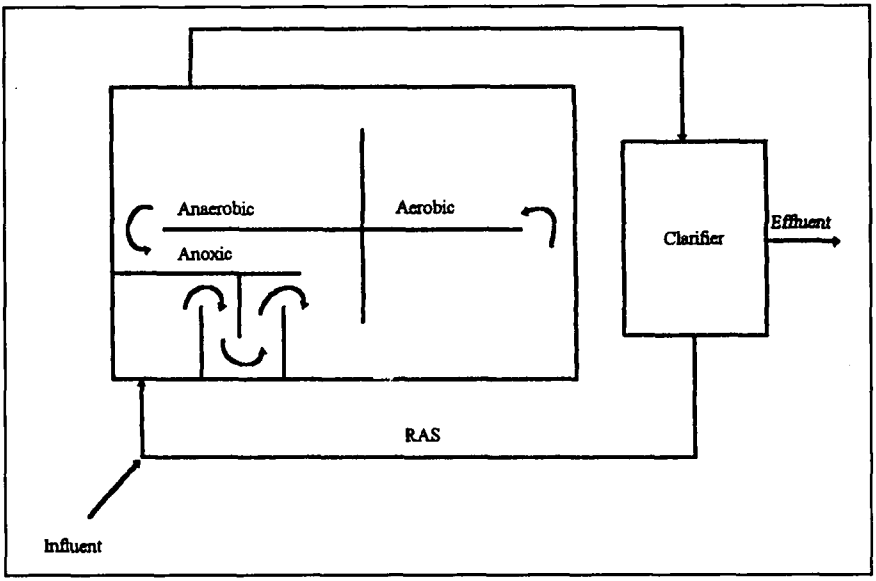

Figure 9. Rotanox process [30].

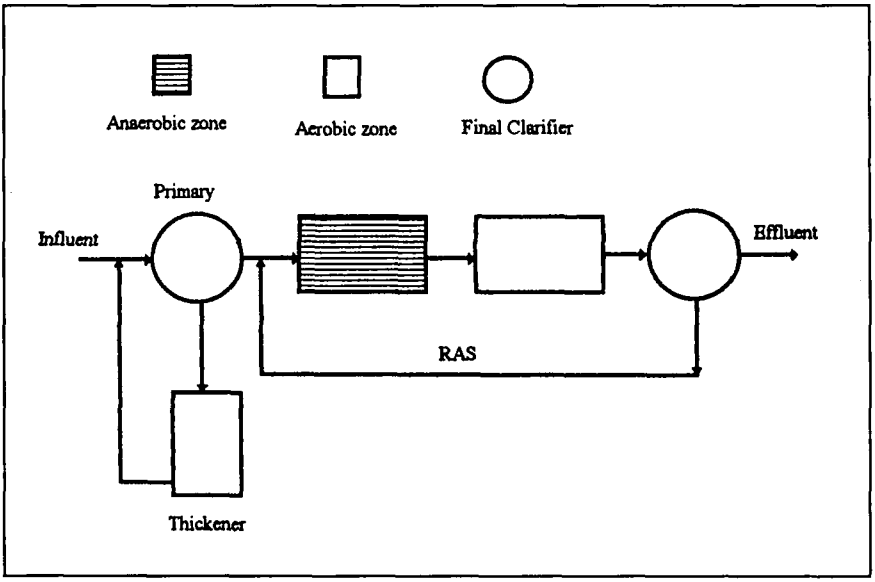

Figure 10. The primary activated process [41].

Table 3. Typical Design Values for Biological Phosphorus Removal Systems [2, 4].

Parameter	A/O Process	PhoStrip Process
F/M, kg/TBOD/ (kg MLVSS)/(d)	0.2-0.7	0.1-0.5
Solids retention time, d	2-25	10-30
MLSS, mg/L	2,000-4,000	600-5,000
Hydraulic retention time, h		
Anaerobic zone	0.5-1.5	8-12
Aerobic zone	1-3	4-10
RAS, %	25-40	20-50
Internal cycle, %	—	10-20

Factors Effecting Process Performance

Limited information is available on the biological phosphorus uptake in the aerobic zone. The available information indicates that for a DO concentration greater than 2 mg/L sufficient phosphorus uptake takes place. Phosphorus removal is not affected by temperatures as low as 10°C, in fact Sell et al. observed higher removals at 5°C than at 15°C [45]. Shapiro et al. indicated that phosphorus release occurred five times faster at 30°C than at 10°C, thus indicating that at low temperatures higher detention time may be required for fermentation to take place [46]. Stirring the contents of anaerobic zones was also found to stimulate the phosphorus release. The optimum pH for biological phosphorus release is in the range of 7.5 to 8.

The presence of NO_x-N in the RAS to the anaerobic zone reduces the process performance [40]. Nitrates consume organic substrate for denitrification which otherwise would have been used for phosphorus release. Tetreault et al. reported that nitrification reduced phosphorus removal efficiency, but only for phosphorus concentrations of less than 1 mg/L in the effluent [47].

Anaerobic contact time is an important parameter for biological phosphorus removal systems. An anaerobic contact time of one to two hours is usually selected [37]. For cultures batch fed with acetate, the organic uptake rate was a function of organic loading to the anaerobic zone, and that two hours was optimum even for higher organic loadings. For aerobic reactors the detention time is not as important as pH and DO concentration. The optimum pH range for effective phosphorus uptake is 6 to 8. The optimum DO levels required for phosphorus removal lie in the range of 2 to 5 mg/L. A fully aerobic zone detention time of one to two hours appeared to be sufficient for phosphorus uptake [37].

The availability of organics is an important parameter for phosphorus removal. The wastewater may not contain enough organics or the organic matter present in the wastewater is not fermented to provide sufficient amount of VFA's needed for the phosphorus release in the anaerobic zone. Gerber et al. noted that phosphate release was controlled by the nature of substrate (short chain VFA's) rather than by the creation of an anaerobic zone [48]. It was also shown that VFA's such as formate, acetate, and propionate were capable of inducing phosphate release under anaerobic, anoxic, and aerobic zones. Organic substrates like glucose, methanol, and citrate also triggered the release, but only after the onset of anaerobiosis. An increase in nitrate concentrations reduced the phosphate release and the uptake under aerobic conditions. Kerrn-Jespersen and Henze indicated that phosphorus uptake was slower under anoxic conditions than under aerobic conditions [49]. A linear relationship was also observed between the amount of acetate taken up under anoxic conditions and the denitrification rate as well as the phosphorus uptake rate under anoxic conditions. COD:TP ratio or BOD_5:TP ratio determines the sizing of an anaerobic basin. If COD:TP ratio is greater than 40:1 and BOD_5:TP ratio is lower than 20:1 then the anaerobic basin size has to be increased. Thus the most important factor is the composition of organic matter present in the wastewater entering the anaerobic zone. Tetreault et al. indicated that PhoStrip process can achieve effluent total P concentration of less than 1 mg/L even at lower BOD_5:TP in comparison to mainstream processes mainly because of the operational flexibility of the sidestream chemical phosphorus precipitation [47].

The experience with full scale biological phosphorus removal systems indicates that effluent TP concentrations of 1 mg/L are not easy to meet. The presence of VFAs in the anaerobic zone plays an important role in phosphorus removal efficiency. It has been shown that the fermentation of primary sludge resulted in VFA concentrations of 110-140 mg/L in fermenter effluent and this upon mixing with influent to the treatment system resulted in the VFA concentration of 9-10 mg/L [50]. The presence of VFA's reduced the effluent phosphorus concentration of 0.5 mg/L. In the modified Bardenpho system phosphate removal was found to increase with the acetate concentration in the anaerobic zone; a correlation coefficient of 0.99 was observed between the two [51]. A solids retention time of about three days was optimum for the maximum conversion of fermentable material [52]. If readily degradable COD in the influent is less than 60 mg/L, excess P removal is unlikely to be achieved in the Phoredox process. For readily degradable COD concentration greater than 60 mg/L, care should be taken to avoid the presence of nitrates in the anaerobic reactor. For a complete nitrification, COD/TKN ratio should be greater than 14 for the Phoredox process to be efficient in phosphorus removal and, for COD/TKN ratio of less than 7, excess biological P removal is highly unlikely. Soluble phosphorus concentrations of less than 0.5 mg/L can be achieved by chemical precipitation of phosphorus [29].

COMBINED NITROGEN AND PHOSPHORUS REMOVAL PROCESSES

A number of biological processes incorporating combinations of anaerobic, anoxic, and aerobic zones have been developed for combined nitrogen and phosphorus removal. The commonly used processes for combined nitrogen and phosphorus removal are A^2/O, Five stage Bardenpho process, UCT, and VIP process.

A^2/O Process

This process is a modification of A/O process described earlier. The process was patented by Air Products and Chemicals, Inc. and is now marketed and licensed by Kruger company. The process provides an anoxic zone with a detention time of approximately one hour. The process can be used for situations requiring only ammonia removal (nitrification) or partial nitrogen removal. The anoxic zone helps to reduce the nitrate loading to the anaerobic zone through the RAS flow (Figure 11). The anoxic zone is usually divided into three equal size complete mix compartments. The mixed liquor is recycled from the end of nitrification stage to the anoxic zone at flows of 100 to 300 percent of influent. The RAS flow ranges from 30 to 50 percent.

A^2/O process nitrogen removal efficiency ranges from 40 to 70 percent and the process has been found to be less effective for phosphorous removal in comparison to the A/O process. An effluent phosphorous concentrations of less than 2 mg/L can be achieved using effluent filtration. The waste sludge has a relatively

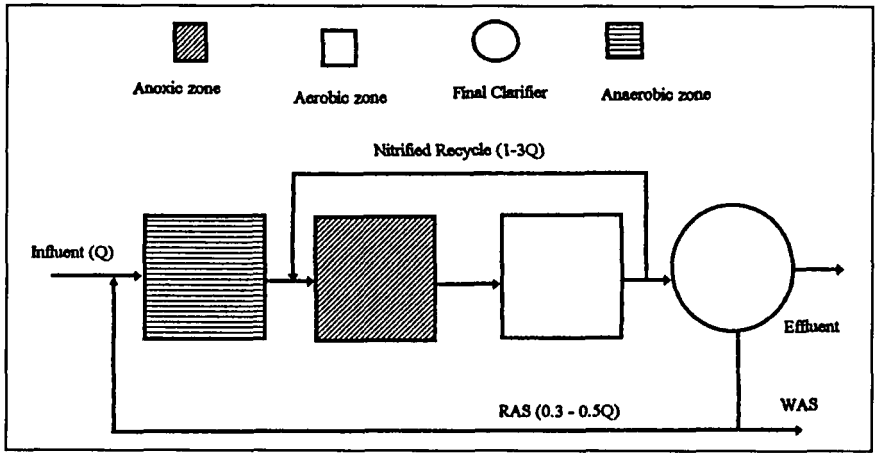

Figure 11. The A^2/O process [4].

higher phosphorus content and thus can be used as a fertilizer. The performance under cold climatic conditions is uncertain and yet to be demonstrated.

Five Stage Bardenpho Process

This process is a modification of the original Bardenpho treatment process [20, 53]. In this process an anaerobic zone at the head of the treatment train is provided. In this process the influent and RAS are contacted in an anaerobic zone to promote fermentation reactions and phosphorus release (Figure 12). In the first anoxic zone, nitrates from the aerobic zone are reduced using influent BOD. In the second anoxic stage, additional denitrification takes place by mixed liquor endogenous respiration. The final aerobic stage prevents the development of anaerobic conditions in the secondary clarifier leading to the release of phosphorus in the final clarifier. The solids retention time is usually in the range of ten to forty days, which is sufficient for sludge stabilization also.

The process is generally designed at low loading rates for nitrogen removal and the rate of operation is slow in comparison to A^2/O. The process is effective to achieve TN effluent concentrations of 3 mg/L or less. The process has demonstrated its capabilities in North America. Bardenpho process has been operating successfully in Kelowna, British Columbia with average effluent values of < 1 mg/L for nitrogen and phosphorus [44]. The process achieved phosphate removals for TKN:COD ratios well below 10 to 1 [54]. The process was designed in 1979 to achieve effluent levels of 2 mg/L TP and 6 mg/L TN. The design values chosen were HRT of twenty-two hours, and SRT of thirty and twenty days for winter and summer conditions, respectively. The process was made more effective and stable over the years. It is now believed that for south-central Canadian

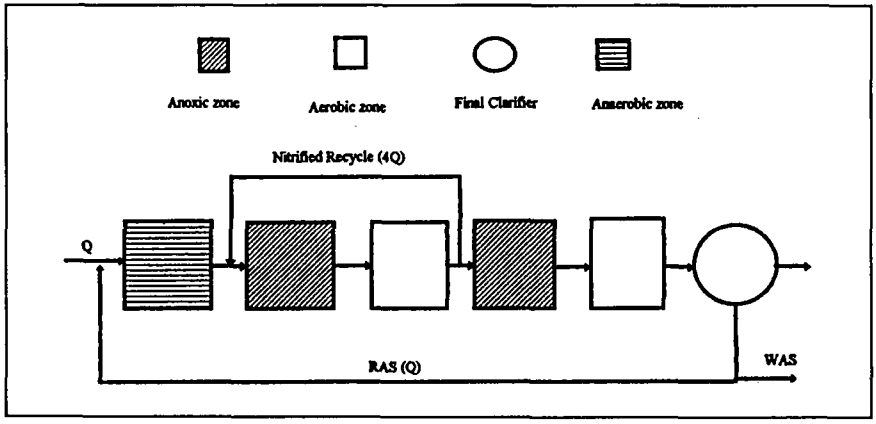

Figure 12. Five stage Bardenpho process [4].

climate the effective N and P removal can be achieved using SRT of twelve to fifteen days in summer and fifteen to twenty days in winter [55]. The presence of primary sludge thickener supernatant in the anaerobic zone was shown to significantly improve the P removal efficiency of the process [44].

UCT Process

This process was developed at the University of Cape Town, and is a modification of the Modified Bardenpho process and resembles the A^2/O process [56]. In this process RAS is returned to the anoxic zone and the internal mixed liquor is recycled from the anoxic zone to the anaerobic zone (Figure 13a). This internal recycle leads to the increased organic utilization in the anaerobic stage due to minimal nitrate concentration in its recycle to the anaerobic zone. The anoxic stage of the UCT process is designed and operated to produce very low nitrate nitrogen. The process is recommended for wastewater with influent TKN:COD ratios greater than 0.08 or COD:TKN ratio of less than 12.0.

The above process was modified by splitting the anoxic zone into two parts (Figure 13b). The first anoxic zone was designed to reduce the nitrate-nitrogen in the RAS and the second zone is designed to achieve even higher nitrate nitrogen removal for the mixed liquor recycled from aerobic zone. The Modified UCT process has not been used in North America, therefore its assessment cannot be made for North American conditions and especially its performance in cold regions. The maximum feasible percent nitrogen removal for Modified UCT process has been shown to be less than 90 percent [4]. The process has less reactor volume than the Bardenpho process. The UCT process can achieve excess P removal if readily biodegradable COD fraction is greater than 60 mg/L and TKN/COD is between 0.11 and 0.14. The modified UCT process is recommended if TKN/COD ratio is in the range of 0.08 to 0.11 [56].

VIP Process

The VIP process resembles A^2/O and UCT processes apart from the methods applied for recycle systems [2] (Figure 14). The RAS and the mixed liquor from aerobic zone are recycled to the inlet of the anoxic zone. The mixed liquor is recycled from the head of aerobic zone to the head of the anaerobic zone, thus reducing the possibility of the presence of nitrates to hamper the anaerobic process. Due to this aspect of the process it is believed that VIP process is relatively less sensitive to the influent wastewater characteristics than other nutrient removal processes discussed above.

The process rate of operation is higher and thus the sizes of reactors are usually smaller than used in the UCT process. The VIP process is usually designed for a solids retention time of five to ten days [57], while the UCT process is designed for ten to thirty days. The VIP process has been reported to possess good nitrogen removal capabilities at low temperatures. The phosphorus removal capacity of

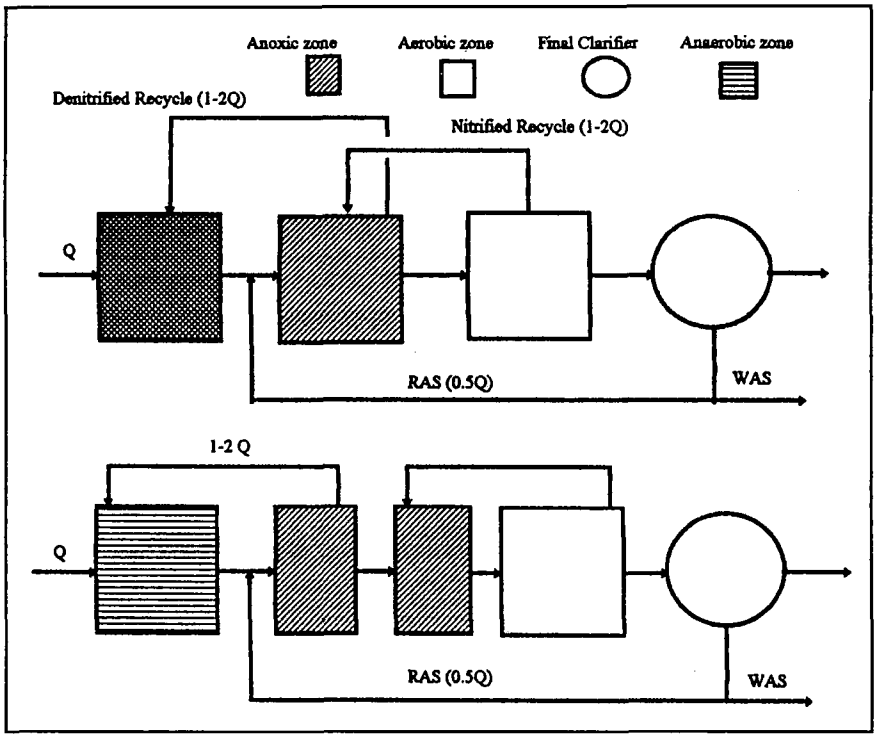

Figure 13. (a) UCT process, (b) modified UCT process [4].

VIP process has been shown to be superior to that of the A^2/O process. The settling and thickening characteristics of sludge produced by the VIP process are relatively inferior in comparison to the sludge produced by A^2/O [57].

Bunnik-Bunschoten (BB) Process

It is a two stage process with alternating aeration [58]. This process is characterized by the activated sludge undergoing anaerobic, anoxic and aerobic phases over time as a result of alternating aeration (Figure 15). During the anaerobic/ anoxic phase the mixed liquor is not mixed but settles on the bottom of the first aeration tank. The supernatant enriched with nitrate does not inhibit P-release in the first aeration tank. The contact time in the first phase must be one to three hours, depending on the wastewater composition and nitrate concentration. Nitrification and denitrification take place in the first and second aeration tanks. During periods of aeration in the first and second aeration tanks *Acinetobacter* accumulates phosphorus.

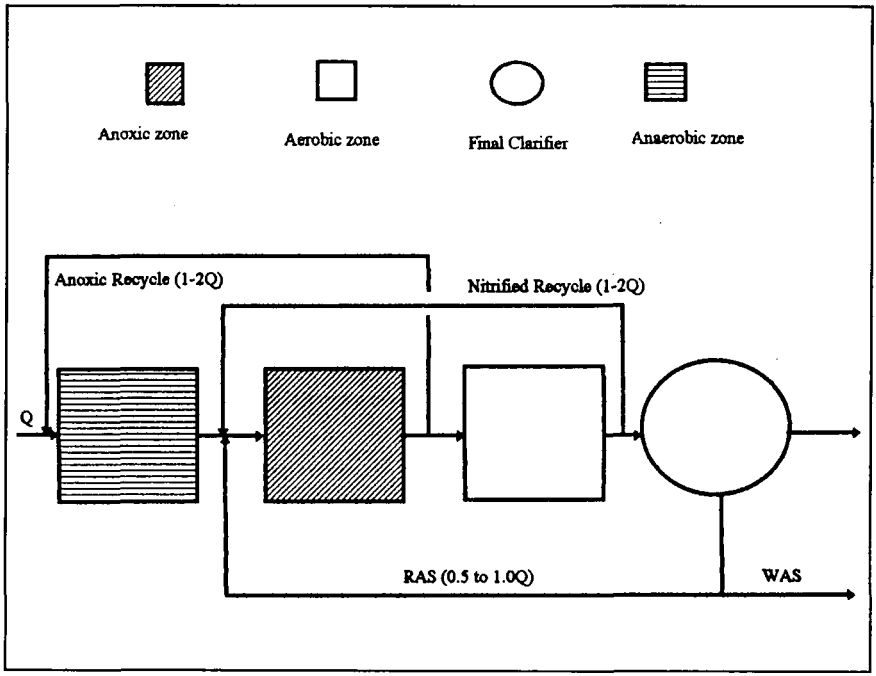

Figure 14. The VIP process [2].

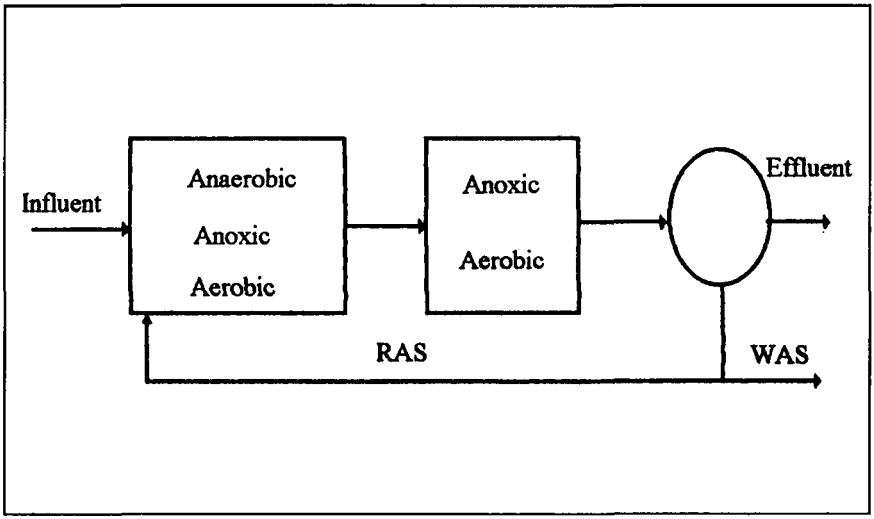

Figure 15. The BB process [58].

Modified Carrousel and Oxidation Ditch

Activated mixed liquor flows continuously around a loop-type channel fitted with an aerator system (Figure 16). With a low oxygenation capacity it is possible to create an aerobic zone capable of nitrification immediately downstream of the aerator and an anoxic zone for some distance upstream of the aerator. By discharging the influent at the upstream limit of the anoxic zone, some of the wastewater carbon source is used for denitrification. By positioning an anaerobic zone in front of the ditch, where the return sludge meets the influent, an optimum combination of phosphorus and nitrogen can be attained. The total phosphorous, ammonia nitrogen and nitrate concentrations in the effluent of 1.1, 0.7, and 2.9 mg/L, respectively, have been recorded at the Bennekom oxidation ditch plant in The Netherlands [58].

POH Process

The process achieves low effluent phosphorus levels through the use of three independently controlled processes (Figure 17). First one is an activated sludge process that uses aeration and solids separation zones and return activated sludge to remove biochemical oxygen demand, phosphorus, and suspended solids. Next unit is a sidestream process for exposure of a portion of the return activated sludge under anoxic conditions to remove dissolved oxygen and nitrates followed by anaerobic conditions to allow selection of desired biological phosphorus removal (BPR) organisms through assimilation of volatile acids and breakdown of stored complex phosphates. Thirdly, a second sidestream process for the fermentation of

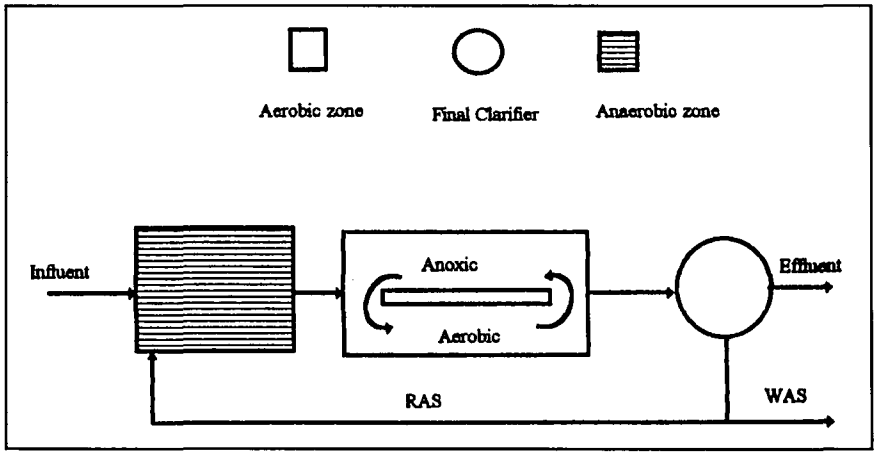

Figure 16. The modified oxidation ditch process [58].

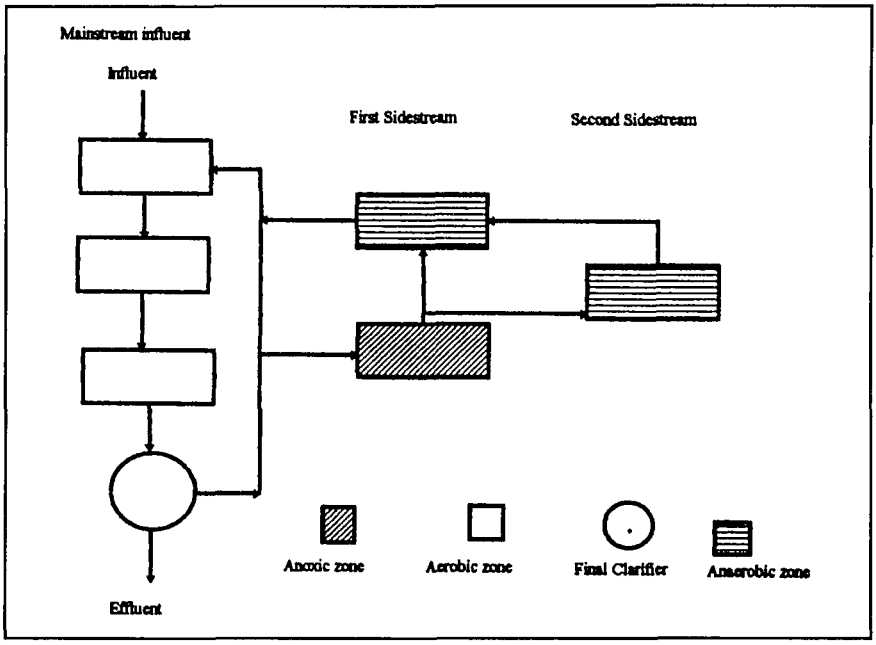

Figure 17. The POH process [59].

organic materials to produce volatile acids and other substances to satisfy metabolic needs of the desired BPR organisms during the selection process is attached.

These three processes are separated from each other through the creation of the sidestream, allowing all the three streams to be controlled separately, optimizing and satisfying the specific goals of each. At Wilson, North Carolina, during the first twelve months of operation the process achieved an average of 0.27 mg/L phosphorus in the effluent [59].

In a recent study biological nutrient removal in intermittent cyclic and continuous activated sludge systems were compared [60]. The modified intermittently fed and decanted system incorporating non-mixing sequences produced an effluent quality of NO_3^--N < 5 mg/L, PO_4^--P < 2 mg/L and NH_3-N < 2 mg/L, with a non-bulking sludge having a sludge volume index < 120 mg/L, despite unfavorable characteristics. In another recent study on BPR in a full scale sequencing batch reactor unit effluent soluble phosphorus concentrations lower than 1 mg/L at water temperatures down to 5°C were observed [61].

Many factors are involved in the selection of a particular process. If moderate nitrogen removal (effluent TN concentration of 6 to 12 mg/L) or only partial nitrification is desired, then A^2/O, UCT, or VIP process can be selected. The selection of the process among the three will be guided by the wastewater

characteristics (readily degradable COD:TP ratio) and effluent phosphorus concentration desired. UCT and VIP processes provide better phosphorus removal than A^2/O process [3]. The Bardenpho process is generally recommended for high nitrogen removal (TN effluent concentrations of 3 mg/L or less). Bardenpho and A^2/O processes are sensitive to the readily degradable COD:TP ratio in comparison with both the UCT and VIP processes.

Design Consideration for Biological Nutrient Removal Processes

Table 4 shows the typical design criteria for the design of combined nitrogen and phosphorus removal processes.

Factors Affecting Process Performance

There are number of factors which can affect the process performance, some of which have already been discussed earlier in this article. In this section some of the design aspects are addressed. Feed wastewater quality plays an important role in the design of a nutrient removal system. The wastewater with a high ratio of TKN:COD does not lend itself to good nitrification. This can have an effect on phosphorus removal due to the presence of nitrates in the recycle which interferes with the production of acetates in the anaerobic basin or the acetate already present will be used for the reduction of nitrates thus inhibiting phosphorus release [44]. Similarly total P: COD (biodegradable) or volatile fatty acids plays an important role in phosphorus removal. It has been shown that when biodegradable COD or VFA concentration is greater than 100 mg/L biological phosphorus

Table 4. Typical Design Criteria for the Nutrient Removal Processes [2, 4]

Design Parameter	A^2/O Process	Bardenpho Process	UCT Process	VIP Process
F/M, (lb BOD)/(lb MLVSS)/(d)	0.15-0.25	0.1-0.2	0.1-0.2	0.1-0.2
Solids retention time, d	4-27	10-40	10-40	5-10
MLSS, mg/L	3,000-5,000	2,000-4,000	2,000-4,000	1,500-3,000
Hydraulic retention time, h				
Anaerobic zone	0.5-1.5	1-2	1-2	1-2
First Anoxic zone	0.5-1.0	2-4	2-4	1-2
Aerobic zone	3.5-6.0	4-12	4-12	2.5-4
Second anoxic zone	—	2-4	2-4	—
Second aerobic zone	—	0.5-1	—	—
RAS, %	20-50	50-100	50-100	50-100
Internal recycle, %	100-300	400	100-600	200-400

removal is easy and for concentrations less than 50 mg/L, special features in the design are demanded [62].

These special design considerations include larger anaerobic zones, special precautions to prevent the nitrate entering the anaerobic zone and fermentation of primary sludge to provide VFA's to the anaerobic zone. The diurnal variations in the characteristics of the feed wastewater can have an impact on the nutrient removal efficiency. Provision of holding tanks can reduce the variations in the influent wastewater. It should be noted that holding tanks should be adequately mixed to prevent settling. Recent evidence indicates that anaerobic stabilization used for biological phosphorus removal stabilizes the organics, and results in reduced oxygen requirement for organic substrate utilization [63]. The results of pilot plant and laboratory studies indicated that reduction of up to 50 percent can occur. Thus the energy expended for aeration can be reduced and thus making the process economical. Wanner et al. reported the advantages of re-aerating the RAS for nutrient removal using modified nutrient removal systems [64]. Higher nitrogen removals were observed for systems utilizing the re-aeration of the RAS.

Two problems that are faced commonly with nutrient removal plants are the bulking of sludges and prolific growth of scum. The problem of bulking sludge can be reduced by preventing the DO level to fall below 1 mg/L in the aerobic zones and controlling the denitrification taking place in the aerobic zones [62]. For high MLSS of 3500-4500 mg/L a stable performance can be achieved by properly designed biological basins and clarifiers [63]. The A/O process was shown to be most effective in terms of bulking of sludges. The extended anaerobic retention time can increase denitrification rates and total P removal, with the sludge volume index of sludges in the range of 50-60 mg/L [66].

The growth of scum forming organisms such as *Microthrix parvicella* and *Norcardia* should be prevented to reduce the scum formation. The growth of these organisms can be prevented by ensuring that surface floating solids or scum layers in the reactors do not reside for a period longer than the total solids retention time of the process. The accumulation of solids behind baffles should be avoided and a free flow should be provided. Special precautions should be taken to ensure that *Norcardia* scum are not recycled into the aeration basins. Traps should be provided to capture the *Norcardia* at the end of the aeration basin [67]. Chlorine spraying of the return sludge can also control foaming. Water sprays have also been used to control foaming.

DISCUSSION

Single-sludge treatment options for biological removal of phosphorus and nitrogen from wastewater have been developed over the past three decades. These processes offer certain advantages over chemical treatment for nutrient removal. These systems use no chemicals and even if chemical dosage is required to meet stringent effluent criteria, dosage is considerably reduced. This reduces the

operating costs due to a decrease in expenditure on phosphorus precipitants. Thus the biological nutrient removal system offers certain distinct advantages over the chemical treatment options for nutrient removal from wastewater.

Single-sludge systems offer a promising approach for nutrient removal from wastewater as indicated by the data currently available from full scale facilities. Morales et al. presented the performance of the Five-stage Bardenpho, A^2/O, A/O and VIP processes from data available in the United States [68]. Table 5 presents the performance of these treatment plants along with the performance of the treatment plant in Kelowna, British Columbia [69], and Calgary, Alberta, Canada [70, 71]. The UCT process was examined for Calgary, but the test results indicated that UCT process exhibited a tendency to become unstable in terms of biological phosphorus removal.

Nitrogen removal is generally more stable and easier to predict with the use of two anoxic zones for producing effluents with TN concentrations ranging from 1 to 3 mg/L. The single anoxic zone process is less effective and it produces effluents with TN concentrations ranging from 4 to 11 mg/L. The removal of phosphorus using established biological nutrient removal processes has been found to be relatively less stable and it has been observed that removal improves with an increase in BOD_5:TPO_4 ratio above 30. For BOD_5:TP ratio of less than 20, Bardenpho, UCT, VIP, A/O and PhoStrip cannot reduce the effluent TP concentration to 1 mg/L without metal salt addition [38]. Wallis-Lage et al. studied the VIP and modified UCT process for nutrient removal from a low strength waste (BOD_5:TP ratio of 13 and BOD_5:TKN ratio of 2.4) [72]. Pilot plant studies showed that phosphorus removal was more a function of the influent BOD_5:TKN

Table 5. Performance of Biological Nutrient Removal Processes [68, 69, 70, and 73].

		TP		TN	
Plant	Type	Influent	Effluent	Influent	Effluent
Largo, FL, US	A^2/O	9.5	2.4	30	7.7
Fayetteville, AR, US	A/O	7.6	1.7	12.9	1.2
York River, VA, US	A/O, A^2/O	9.2	3.3	29	14.9
York River, VA, US	VIP	6.7	1.5	27.8	12
East Boulevard, MN, US	A/O	3.2	0.6	22.5	13.3
Virginia, US	VIP	5.2	1.2	25	7.7
Kelowna, B.C., Canada	Bardenpho	3.8	0.15	22[a]	1
Calgary, Alberta, Canada	3 stage Bardenpho	6.87	0.45	18.39[a]	2.50
Palmetto, FL, US	Bardenpho	6.5	0.6	32	2.5
East Service Area, FL, US	Bardenpho	8.2	0.7	31	1.8
Buenaventure, FL, US	Bardenpho	9.1	0.29	39	1.9

[a]Ammonia

ratio; for BOD_5:TKN ratio of less than 2.4 phosphorus was limited. For BOD_5:TP of less than 20, US EPA recommends VIP or UCT process over A^2/O or Bardenpho process [4]. Effluent filtration can also reduce the effluent phosphorous concentrations [29]. Morales et al. observed that effluent filtration exerted minimal influence on phosphorus removal performance, though effluent filtration provided a measure of protection against scenarios of total suspended solids carryover [68]. Solids handling, recycling and nitrification can reduce the phosphorus removal efficiency due to the presence of nitrates in the recycle. The VIP process has been shown to offer a better performance in a nitrifying mode. Biological phosphorus removal is less stable and consistently low effluent concentration can be achieved by chemical treatment (alum, lime, or ferric chloride) of effluent or addition of short chain VFA's to influent in the anaerobic zone [74]. Table 5 shows that Bardenpho process provides efficient nutrient removal and the process has worked well in the colder climate of Canada. The VIP process is also able to achieve low phosphorus effluent concentrations and is more effective than A/O and A^2/O when operating in a nitrifying mode.

The selection of a particular process for a particular case will depend on a large number of factors. The facilities operating at the existing plant to be retrofitted or type of existing plants, climatic conditions, wastewater characteristics, and cost-effectiveness govern the applicability and process to be selected. Cooper et al. provided a summary of various processes to achieve the effluent criteria stipulated generally [74]. Table 6 highlights their findings with respect to the nutrient removal processes discussed in this article.

Table 6. Nutrient Removal Processes to Meet Low Nutrient Criteria [38, 74]

	Total Phosphorus Concentration						Total Nitrogen Concentration	
	1 mg/L			2 mg/L			10 mg/L	15 mg/L
Process	W	CA	CAF	W	CA	CAF	W	W
PhoStrip	Y			Y				
PhoStrip	Y			Y			Y	Y
A/O	V	Y	Y	V	Y	Y	N	N
A^2/O	V	Y	Y	V	Y	Y	V	V
Bardenpho	V	Y	Y	V	Y	Y	Y	Y
VIP	V	Y	Y	V	Y	Y	Y	Y
UCT	V	Y	Y	V	Y	Y	Y	Y

Notes: W = without any chemical addition and filtration, CA = chemical addition, CAF = chemical addition and filtration, Y = meets the criteria, N = will not meet the criteria, V = will meet the criteria depending on influent.

CONCLUSIONS

The extensive research on biological nitrogen and phosphorus removal for the past two decades has led to the development of various biological nutrient removal processes. These processes, in particular the modified activated sludge processes offer distinct advantages over physico-chemical treatment methods for nutrient removal and are gaining wider acceptance. The operating data from treatment plants utilizing the processes discussed in this review indicate their effectiveness in nutrient removal from wastewater. Bardenpho process has been found to operate effectively under the cold Canadian climatic conditions.

Biological nitrogen removal has been found to be relatively more stable in terms of operation and control than phosphorus removal. Feed wastewater characteristics seems to play an important role in nutrient removal processes. The presence of VFA's in anaerobic zone determines the extent of phosphorus removal. The COD:TKN ratio is an important parameter for nitrogen removal. Modified activated sludge processes for nutrient removal demand strict monitoring of the process in comparison to conventional activated sludge plants, especially if high phosphorus removals are desired. Two common problems usually faced with nutrient removal plants are scum formation and bulking of sludges; various options are available to control these problems. An important factor in overall effectiveness of the treatment process is the careful handling and treatment of phosphorus-rich sludges, so that phosphorus recycle is minimized. At present limited cost information is available for the direct comparison of the various processes discussed in this article to determine their cost effectiveness.

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