

A Review of Anoxic Wastewater Treatment: An Overlooked Aspect in Wastewater Treatment in Nigeria

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Abstract This paper presented an overview of different methods for nitrogen and phosphorus removal from wastewater effluents in Nigeria. Research data indicated that wastewater effluents in Nigeria contain high concentrations of nitrogen and phosphorus, which contributed to the eutrophication of many surface water bodies in the country. Study of wastewater characteristics in Nigeria showed that wastewater effluents in Nigeria contain an average of 650mg/l of total nitrogen, 120mg/l of total phosphate and 55,000mg/l of COD; nitrate-nitrogen and phosphorus ranged between 43mg/l and 56mg/l; ammonium nitrogen ranged between 52mg/l and 107mg/l; nitrate nitrogen from ranged 34.5mg/l and 58.5mg/l. The technologies and principles of anoxic treatment of wastewater are presented. The stoichiometry of nitrification and denitrification reactions are presented. State and Federal Ministry of Environment in Nigeria should enforce relevant regulations to ensure that wastewater effluents are treated to reduce nitrogen and phosphorus content to acceptable standards before discharge into watercourses.

Keywords: *nitrogen, phosphorus, eutrophication, chemical precipitation, biological removal, nitrification-denitrification, stoichiometric equations, wuhrmann system, ludzack-ettinger system, bardenpho 4-stage process*

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1. Introduction

The improper management of domestic and industrial wastewater in Nigeria poses a big threat to the aquatic environment. Different types of wastewater are generated from both domestic and industrial activities [1]; domestic sources include cleaning, bathing, washing, cooking, and so on [2]. Industrial wastewater effluents are generated by chemical industries (refineries, petrochemical plants, etc.), food and beverage industries, textile industries, and so on [3]. These wastewater effluents contain high concentrations of biological oxygen demand (BOD), and chemical oxygen demand (COD), including nutrients such as ammonia, nitrates, nitrites and phosphorus [1]. In Nigeria, wastewater effluents (domestic and industrial) are often discharged into canal, rivers, and streams with little or no treatment. The main objective of wastewater treatment in Nigeria today is to reduce the amount of organic matter and suspended solids in wastewater. Hence, some wastewater effluents are treated to reduce only the BOD contents with little or no consideration for nitrogen and phosphorus removal. The discharge of these nutrients loaded wastewater effluents into surface water bodies not only deteriorate the quality of the water but also encourage the excessive growth aquatic plants such as algae and water hyacinths leading to a condition known as eutrophication of surface waters [1,4].

2. Overview of Wastewater Treatment Process

Wastewater treatment consists of the following processes as shown in Figure 1.

1. Preliminary treatment
2. Primary treatment
3. Secondary treatment
4. Tertiary (advanced) treatment

Preliminary treatment removes materials that cause operational problems in the treatment process. It involves the use of bar screens, grit removal, oil-water separators and flow equalization [5]. During this phase, large solid objects such as sticks, rags, grit, plastics, concrete, wood and debris that may clog piping and damage pumps are removed [5].

Primary treatment is the second step in wastewater treatment that involves gravity settling tanks to remove settleable solids and organics. Suspended solids and settleable organic solids such as grease are physically separated from the wastewater [5]. It removes about 60% total suspended solid (TSS) and 35% biochemical oxygen demand (BOD) from wastewater [6]. It consists of primary settling tank (PST) where the wastewater is held for several hours to allow solid particles to settle to the bottom of the tank while oils and greases float to the top.

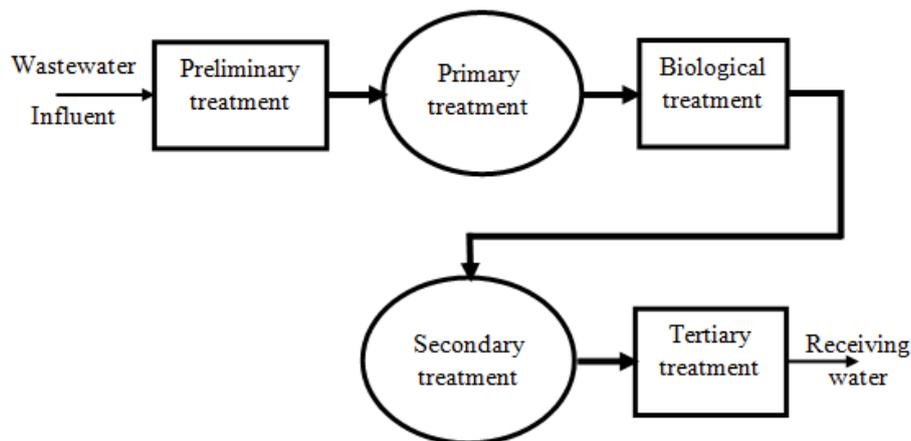


Figure 1. Flow diagram of the wastewater treatment system

Secondary treatment is the biological treatment of wastewater to remove colloidal and soluble organic matter [5]. It follows primary treatment and removes about 85% BOD from wastewater. Two methods are used in secondary treatment of wastewater:

- i. Suspended Growth (suspended organisms)
 - Activated sludge
 - Oxidation ditches/ponds
 - Aerated lagoons, stabilization ponds
- ii. Fixed Growth or Biofilms (attached organisms)
 - Trickling filters
 - Rotating Biological Contactors

Tertiary or advanced treatment is the final treatment of wastewater before discharge into the receiving water body. It involves physical, chemical or biological treatment of wastewater to remove trace organics (BOD), colour, solids, nitrogen and phosphorus. Advanced treatment removes more than 95% of BOD, solids, nitrogen and phosphorus from wastewater [6].

3. Necessity for Anoxic Treatment of Wastewater

Nitrogen and phosphorus are essential nutrients for the growth of aquatic plants such as algae and water hyacinths. The excess concentrations of these nutrients in the receiving water bodies leads to dense growth of the aquatic plants such as algae and water hyacinths resulting in a condition called eutrophication [1,4,5,7]. The phenomenon of eutrophication usually decreases water quality by reducing its dissolved oxygen (DO) content and thus affecting aquatic life [5,7]. The decomposition of dead aquatic plants by microorganisms depletes the dissolved oxygen (DO) in the receiving water bodies below critical conditions, leading to the death of aquatic life. The main objective of anoxic treatment is to remove nitrogen and phosphorus from wastewater effluent before discharge into receiving water body [8]. Hence, to prevent eutrophication of rivers and streams, there is need for anoxic treatment of wastewater to reduce nitrogen and phosphorus concentrations in the effluent to acceptable standard before discharge in surface waters. The Federal Government has set standards for wastewater effluent discharge into watercourses in Nigeria as follows [9]:

Nitrite - N	-----2.0 mg/l
Nitrogen total	-----10 mg/l
Phosphate (soluble)	-----5.0 mg/l
Total phosphate	-----10mg/l.

3.1. Pro and Cons of Anoxic Treatment

The removal of nutrients improves the operation of the treatment plant; it increases sludge density and reduces the growth of filamentous organisms due to absence of oxygen; less sludge is produced as nitrate produced in the anoxic zone can be used for BOD removal in the aerobic zone. However, anoxic treatment causes the release of greenhouse gas, nitrous oxide (N_2O), into the atmosphere; it also requires enormous amount of energy [10,11].

4. Sources of Nitrogen and Phosphorus in Wastewater

Nitrogen exist in wastewater in the form of organic nitrogen ammonia (NH_3), ammonium ion (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-) and organic nitrogen [5] of these, approximately 30 to 40% are organic nitrogen and 60 to 70% are ammonia-nitrogen [5,12]. Similarly, Phosphorus exists in wastewater as either phosphate (Orthophosphate) or polyphosphate, or organically bound phosphorus [5]. The main sources of nitrogen and phosphorus in wastewater are human and animal wastes (excreta), food preparation, and use of fertilizer, detergents, and other cleaning agents [1,5,7,12].

Studies indicated that wastewater in Nigeria contains high concentrations of nitrogen and phosphorus, [13] reported nitrate-nitrogen and phosphorus concentrations in wastewater that ranged from 43 to 56mg/l. Ammonia-nitrogen (NH_3-N) of 27.65mg/l has been reported in domestic wastewater in Port Harcourt [14]. A chemical oxygen demand (COD) up to 1254.50mg/l has been reported in industrial wastewater effluent in Lagos [15]. A study of wastewater characteristics in South Eastern Nigeria found average ammonium nitrogen between 52mg/l and 107mg/l; nitrate nitrogen from 34.5mg/l to 58.5mg/l; phosphate (PO_4^{3-}) [16]. Wastewater effluent from a palm oil mill in Nigeria was found to contain an average of 650mg/l of total nitrogen, 120mg/l of total phosphate and 55,000mg/l

of COD [17]. These values exceeded the Nigerian effluent discharge standard as stipulated by The National Environment (Standards for Discharge of Effluent into Water or on Land) Regulations, 1999 [9]. A snapshot of local people bathing in a river infested with aquatic plants in Rivers State, Nigeria is shown in Figure 2. Thus, wastewater in Nigeria requires treatment for nitrogen and phosphorus removal before discharge into watercourses. This paper therefore, attempts to review anoxic wastewater treatment which is an overlooked aspect in wastewater treatment in Nigeria. The paper provides an overview of different methods and technologies employed for nitrogen and phosphorus removal from wastewater.



Figure 2. Locals bathing in a River Infested with Aquatic Plants in Rivers State, Nigeria (Field snapshot, August 2019)

5. Anoxic Wastewater Treatment

This is the chemical and biological treatment of wastewater that reduces nitrate, phosphorus and other residual organics and solids in wastewater effluent after primary and secondary treatment [2].

5.1. Principles of Phosphorus Removal

The objective is to reduce excess phosphorus in wastewater to acceptable standards before discharge into receiving water bodies. Primary treatment of wastewater removes about 15% of total phosphorus by sedimentation [18]. Conventional removal involves the transfer of soluble phosphorus to a solid phase followed by solid-liquid separation [7]. Conventional methods of phosphorus removal include [7] chemical phosphorus removal, biological phosphorus removal, and a combination of both.

Chemical precipitation (addition of salt [19] is the most common method used to remove phosphorus from wastewater [5]. The method is used simultaneously with biological phosphorus removal (BPR) to reduce the costs of chemical dose and sludge production. Chemical precipitation of phosphorus can be done at the primary or secondary clarification, or advanced/tertiary filtration stage of the wastewater treatment. Chemicals can be applied as direct precipitation, pre-precipitation, simultaneous precipitation or post-precipitation. Metal salts or lime are chemicals typically used for phosphorus precipitation [5,20]. Commonly used chemical salts are aluminum sulphate or alum $[Al_2(SO_4)_3]$, ferric chloride $[FeCl_3]$, sodium aluminate $[Na_2Al_2O_4]$, polyaluminum chloride

(PAC) $[Al_nCl_{(3n-m)}(OH)_m]$, ferrous sulphate (Iron 11 sulphate) $[Fe_2SO_4]$ and quicklime (CaO) or hydrated lime $Ca(OH)_2$.

Only the phosphate portion of the total phosphorus in wastewater can be removed by chemical precipitation [5]. Phosphate is between 50 and 80% of total phosphorus in wastewater and exists in either as $H_2PO_4^{4-}$ or HPO_4^{2-} [5]. Polyphosphates cannot be removed by chemical precipitation as they do not react with metal salts or lime, however, they are converted to phosphate during biological phosphorus removal. The organic fraction of phosphorus in wastewater is less than one milligram per liter ($1 < mg/L$) of the total influent phosphorus. Soluble organic fraction of phosphorus may either be hydrolyzed into orthophosphate during biological treatment or will pass through the treatment plant if there is no biological treatment [5].

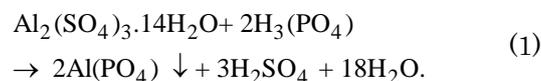
5.1.1. Stoichiometric Equations Phosphorus Removal Using Metal Salts

Critical design and economic factors that affect the phosphorus removal efficiency of chemical precipitation treatment systems are:

- i. Metal salt dose
- ii. Wastewater characteristics,
- iii. Method of chemical addition,
- iv. Chemical addition feeding point(s),
- v. Reaction pH,
- vi. Flocculation method, and
- vii. Time after chemical addition

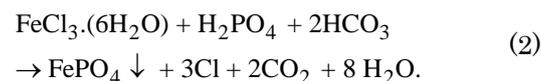
The metal salt dose (Me_{dose}) is defined as the moles of metal added per mole of soluble phosphorus in the influent (P_{ini}) [5].

The stoichiometric dose is the molar ratio requirement for purely a chemical reaction between metal salts and soluble phosphorus in the influent to form a precipitate (M-PO₄). It is 1.0 mole of metal salts added per mole of phosphorus removed (i.e., $1.0 Me_{dose}/P_{ini}$) [5]. The stoichiometric equations for the chemical reactions are given in the following expressions [5,21]. Phosphorus removal using Aluminum sulphate or alum $[Al_2(SO_4)_3]$ is given as:



According to Equation (1) Aluminum phosphate (ALPO₄) solid is precipitated and removed out of the wastewater effluent.

Phosphorus removal using Ferric chloride $[FeCl_3]$ is given as:



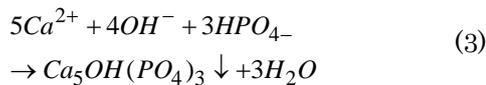
According to Equation (2) Iron phosphate (FePO₄) solid is precipitated and removed out of the wastewater effluent.

Study [22] found that about 80 to 98% of soluble phosphorus can be removed with ferric doses above 1.5 to 2.0 Me_{dose}/P_{ini} ratios. Similarly, alum dose ratios of about 6 or 7 Me_{dose}/P_{ini} have been reported to remove about 75 to 95% of phosphorus from wastewater [21]. Factors that affect metal dose and phosphorus removal efficiency

include initial mixing conditions, pH, chemical oxygen demand (COD) in the wastewater, total suspended solids (TSS) and flocculation [5,23,24]. Polymers can be added to the metal salts to enhance removal for fine particles and colloids during phosphorus precipitation [5].

5.1.1.1. Stoichiometric Equations Phosphorus Removal Using Lime

Phosphorus is removed from wastewater by adding lime (CaO) or Ca(OH)₂. The lime first react with alkaline bicarbonate in the wastewater to form calcium carbonate (CaCO₃). Increase in the pH causes excess ions in the wastewater to react with phosphate to form hydroxylapatite [Ca₅(OH)(PO₄)₃] which is precipitated out as shown in Equation (3) [5].



According to Equation (3) hydroxylapatite [Ca₅(OH)(PO₄)₃] solid is precipitated and removed out of the wastewater effluent.

5.1.1.2. Observations

- i. Lime dose does not depend on influent phosphorus concentration [5]
- ii. Lime dose is typically 1.4 to 1.6 times the total alkalinity expressed as CaCO₃ [12].
- iii. Lime raises the pH of the wastewater to greater than 11 [5]
- iv. Lime cannot be added directly to biological treatment processes, which requires pH levels below 9 [5].
- v. Lime has been found to produce a much greater volume of sludge compared to metal salts
- vi. Lime can cause scaling in mechanical thickening and dewatering systems.
- vii. Alum produces less sludge than ferric salts.
- viii. Alum sludge can be more difficult to concentrate and dewater compared to ferric sludge.
- ix. The use of metal salts can result in increased inorganic salts (salinity) in the sludge and in the effluent.
- x. High total salts can reduce germination rates for crops and negatively affect the soil structure, in addition to potential taste and odor problems when the sludge is applied to land.
- xi. An advantage of lime sludge is that some stabilization can occur due to the high pH levels required

The amount of solid precipitates from the wastewater effluent determines the efficiency of phosphorus removal by methods of chemical precipitation. The solids can be separated from the effluent by gravity separation in primary and/or secondary clarifiers [5]. Flocculation zones in secondary clarifiers can be used for solid removal. Tertiary filtration after secondary clarification is carried out polishing stage to reduce TSS concentrations in the effluent to below 0.50 mg/l [5].

5.1.1.3. Disadvantages of Phosphorus Removal chemical Methods

Produces additional solids due to the generation of metal- or calcium- phosphate precipitates and metal hydroxide sludge [5,21]. The total overall plant sludge

production in the primary treatment increases by 60 to 70% [21] due to phosphorus and hydroxide precipitates and increased suspended solids removal. The overall plant sludge production in the secondary treatment may increase by 5 to 25% [21]. The sludge production for the secondary/tertiary treatment may increase 45 to 60%. The total overall sludge production may increase by 10 to 40% for the wastewater treatment plant (WWTP).

Two factors that may limit the ability of plants to achieve very low effluent levels

Some portion of phosphorus in wastewater influence such as organic phosphorus and dissolved acid-hydrolyzable phosphorus can be recalcitrant and remain unchanged after treatment [25,26]. It is also difficulty to measure very low concentrations of phosphorus (< 0.020 mg/l) in effluent [21,27].

5.1.2. Biological Phosphorus Removal (BPR)

BPR existing technologies include treatment plants without nitrogen removal (side stream and recirculation processes), and treatment plants with nitrogen removal (alternating and recirculation processes) [5,28]. Biological phosphorus removal is accomplished using phosphorus accumulating organisms (PAOs). These microorganisms are heterotrophic bacteria such as *Acinetobacter* species, *Pseudomonas*, *Arthrobacter globiformis* and *Klebsiella pneumonia* that exist in the environment and in aerobic activated sludge [5,7]. The PAOs are recycled between aerobic and anaerobic conditions to enhance their growth.

In the BPR process, PAOs store a large mass of phosphorus in their cells in the form of polyphosphates (energy). The storage of polyphosphates occurs in the aeration zone where oxygen is utilized by the microorganisms. Under anaerobic conditions (absence of oxygen), the PAOs break down the polyphosphates into volatile fatty acids (VFAs) which are stored as poly-β-hydroxy-alkanoates (PHAs) called poly-β-hydroxy-butyrate (PHB) [5,7]. Again, when oxygen is available the PAOs metabolize the PHAs to generate energy and uptake phosphorus (in the form of phosphate) and store the excess amount.

The main steps involves in biological phosphorus removal are shown in Figure 3. First, the recycled activated sludge containing PAOs from the secondary clarifier is added to the influent wastewater. Secondly, in the anaerobic zone, PAOs break polyphosphate bonds to generate energy and release phosphate ions (PO₄⁻³) in their cells. The energy is used to absorb VFAs and store them as PHA compounds (PHB). Thirdly, in the aerobic zone, the PAOs in the wastewater and return sludge use oxygen to metabolize the stored PHAs to generate energy for growth. At the same time more phosphate ions are absorbed along with magnesium, potassium, and other positive ions to form polyphosphates which are stored as excess energy. Fourthly, as the wastewater flows into the clarifier, the PAOs settle out to the bottom together with the activated sludge and removed together with the phosphorus stored in the PAOs. The process result in a net removal of phosphorus during wastewater treatment. However, phosphorus removal by chemical precipitation is at present the best known process and is widely used despite its relatively high costs.

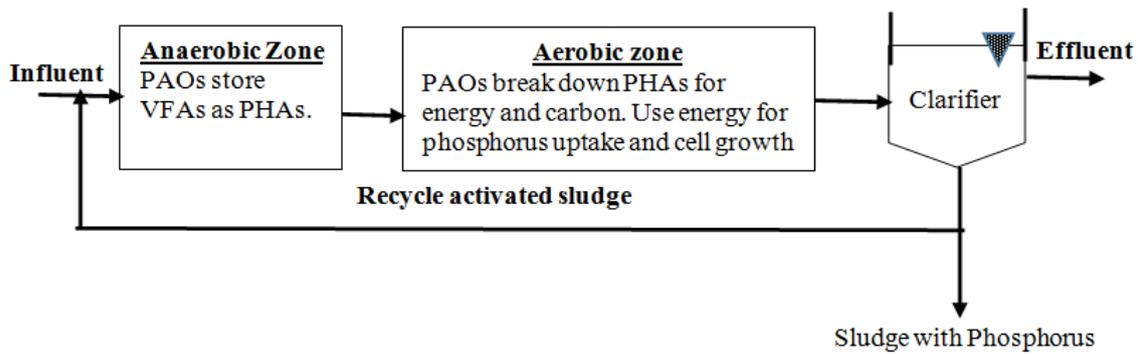


Figure 3. Biological phosphorus removal process [5]

5.2. Biological Nitrogen Removal in Wastewater

Biological nitrogen removal in wastewater involves the use of microorganisms to remove nitrogen content in wastewater to acceptable level before discharge into a water course. Two primary technologies are involved in the biological treatment of wastewater to remove nitrogen [5].

1. Nitrogen assimilation (biomass synthesis) and sludge wasting, and
2. Biological nitrification and denitrification,

5.2.1. Nitrification Process

Two stages are involved in nitrification process: first aerobic bacteria such as Nitrosomonas oxidize or convert ammonia-nitrogen ($\text{NH}_3 - \text{N}$) to nitrite-nitrogen ($\text{NO}_2 - \text{N}$), and second bacteria such as Nitrobacter convert $\text{NO}_2 - \text{N}$ to nitrate-nitrogen ($\text{NO}_3 - \text{N}$). The conversion of ammonia-nitrogen to nitrate-nitrogen occurs in an aerated suspended growth system or aerobic treatment process such as a trickling filter.

5.2.2. Nitrogen Removal by assimilation or Biomass Synthesis

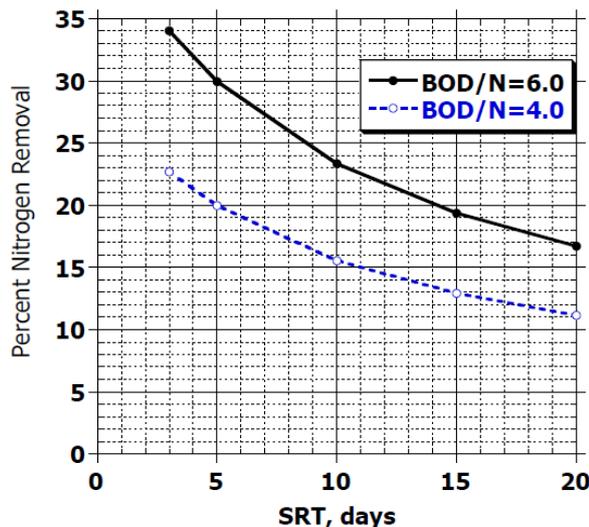


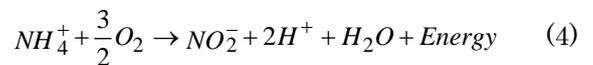
Figure 4. Effect of influent BOD/TN and SRT ratio on nitrogen removal efficiency [5]

About 10 to 30% of influent nitrogen is removed during convention treatment of domestic wastewater for biochemical oxygen demand removal [5]. Autotrophic

bacteria (ammonia-oxidizing) such as Nitrosomonas, Nitrosococcus and Nitrospirilla convert ammonia to nitrite and use dissolved oxygen to oxidize inorganic ammonia compound to get cell energy [29]. The efficiency of nitrogen removal depends on the influent BOD to total nitrogen (TN) (BOD/TN) ratio and the solid retention time (SRT). The percent of nitrogen removal due to biomass synthesis is a function of SRT and influent BOD/N ratio. Relationship between nitrogen removal and solids retention time (SRT) and BOD/N ratio is shown in Figure 4.

5.2.3. Reactions and Stoichiometry of Nitrification

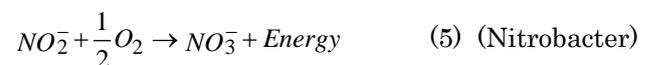
Two steps are involved in the biological process (Figure 5), the first step is the oxidation reaction by ammonia-oxidizing bacteria (AOB) to yield energy as given in Equation (4) [5,30]:



(Nitrosomonas)

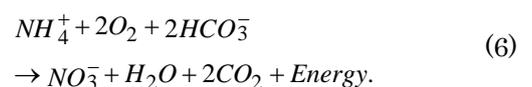
From Equation (4) 1.5 moles of oxygen is required to oxidize 1 mole of ammonia and produced 2 moles of hydrogen.

The second step is the oxidation of nitrite ($\text{NO}_2 - \text{N}$) to nitrate - nitrogen ($\text{NO}_3 - \text{N}$) by nitrite - oxidizing bacteria (NOB) called Nitro - organisms [29,30] as expressed in Equation (5).



From Equation (5) 0.5 moles of oxygen is required to oxidize 1 mole of nitrite and produced 1 moles of nitrate. Also, 1.14g of O_2 is required to oxidize $\text{NO}_2 - \text{N}$ to $\text{NO}_3 - \text{N}$.

The overall stoichiometry reaction for the complete nitrification process can be expressed as follows:



5.2.3.1. Mass Stoichiometry with NH_4^+ as the Reference Compound

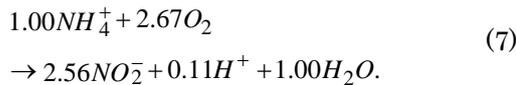
From Equation (4), the mass of oxygen required to oxidize $\text{NH}_4 - \text{N}$ to $\text{NO}_2 - \text{N}$ is computed as

$$1.5 \text{ O}_2 = 1.5 \times 32 = 48\text{g}$$

$$\text{Mass of O}_2 \text{ required} = 48/14 = 3.43\text{g}.$$

Therefore in the first step, $\text{NH}_4 - \text{N}$ to $\text{NO}_2 - \text{N}$ required 3.43g O_2 $\text{NH}_4 - \text{N}$.

The stoichiometry of Equation (4) can thus be written as:



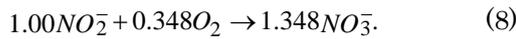
From Equation (5), the mass of oxygen required to oxidize NO₂-N to NO₃-N is determined as follows:

$$0.5O_2 = 0.5 \times 32 = 16g$$

$$\text{Mass of } O_2 \text{ required} = 16/14 = 1.14g$$

Therefore in the second step, NO₂-N to NO₃-N required 1.14g O₂/NO₂-N.

The stoichiometry of Equation (5) can thus be written as:



From the overall Equation (6), the total O₂ required for the complete nitrification process is 3.43 + 1.14 = 4.57g.

Alternative, it can be determined as follows:

$$2O_2 = 2 \times 32 = 64g$$

$$\text{Mass of } O_2 \text{ required} = 64/14 = 4.57g.$$

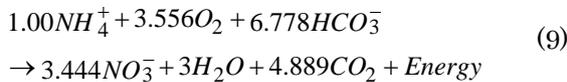
Therefore, the complete ammonia oxidation to nitrate required 4.57g O₂/NH₄-N.

The amount of alkalinity (as CaCO₃) consumed per gram of NH₄-N oxidized is computed as:

$$CaCO_3 = 40 + 12 + 48 = 100g$$

$$\text{Mass of } CaCO_3 \text{ consumed} = 100/14 = 7.14 g.$$

The stoichiometry of Equation (6) can thus be written as:



From the above stoichiometry:

- a. 4.57g O₂/NH₄ - N is utilized
- b. 7.14g as CaCO₃ (alkalinity) is consumed
- c. 1g NO₃-N is generated

Nitrification

$$\rightarrow 7.14 \frac{\text{g of alkalinity as } CaCO_3 \text{ reduced}}{\text{g } NH_4\text{-N oxidized}} \quad (10)$$

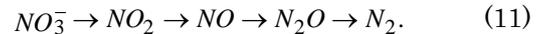
The above result is based only on oxidation and does not include cell synthesis for biomass Growth. It is therefore a conservative result suitable for practical design

estimates [12,30]. When AOBs utilize ammonia for biomass growth (cell synthesis) then the result will be lower as follows [30]:

- a. 4.45g O₂/NH₄ - N is utilized
- b. 7.11g as CaCO₃ (alkalinity) is consumed
- c. 0.99g NO₃-N is generated

5.2.3.3 Denitrification

Denitrification is the biological reduction of nitrate or nitrite and convert to nitrogen gas (N₂) in wastewater treatment processes [5]. Denitrification is achieved by a broad wide range of heterotrophic facultative bacteria which use nitrate, or nitrite as their terminal electron acceptors for the oxidation of organic material. In anoxic conditions, the bacteria use nitrate (NO₃⁻) or NO₂ (nitrite) as electron acceptor instead of oxygen [5,30]. Heterotrophic bacteria are primarily responsible for denitrification in the biological nitrification-denitrification processes of wastewater treatment. The biological denitrification of BOD in influent wastewater is accomplished by facultative aerobic bacteria (FAB) which use elemental oxygen, nitrate, or nitrite as their electron acceptors for the oxidation of organic material [5,30]. They make use of oxygen as the electron acceptor when it is present and in the absence of oxygen they use nitrate, or nitrite. The denitrification process to reduce nitrate in wastewater involves the oxidation of nitrate (NO₃⁻) to nitrite (NO₂⁻), nitric oxide (NO); and nitrous oxide (N₂O) to nitrogen gas (N₂) as expressed in the equation below.



Sources of soluble organic substrate (electron donors) used for denitrification of influent wastewater are:

- i. The soluble degradable COD in the influent wastewater (internal electron donor present in wastewater)
- ii. Degradable COD produced during endogenous decay (self-generated electron donor via endogenous respiration)
- iii. External source such as methanol (external electron donor dosed to system)

Hydrolysis of biodegradable particulate and colloidal COD in the influent wastewater. In the biological removal of nitrogen from wastewater, supplemental carbon source is required to:

- i. provide sufficient carbon for nitrate/nitrite reduction
- ii. provide sufficient carbon for nitrate/nitrite reduction
- iii. provide a carbon source for further nitrate/nitrite reduction in post-anoxic systems such as denitrification filters.

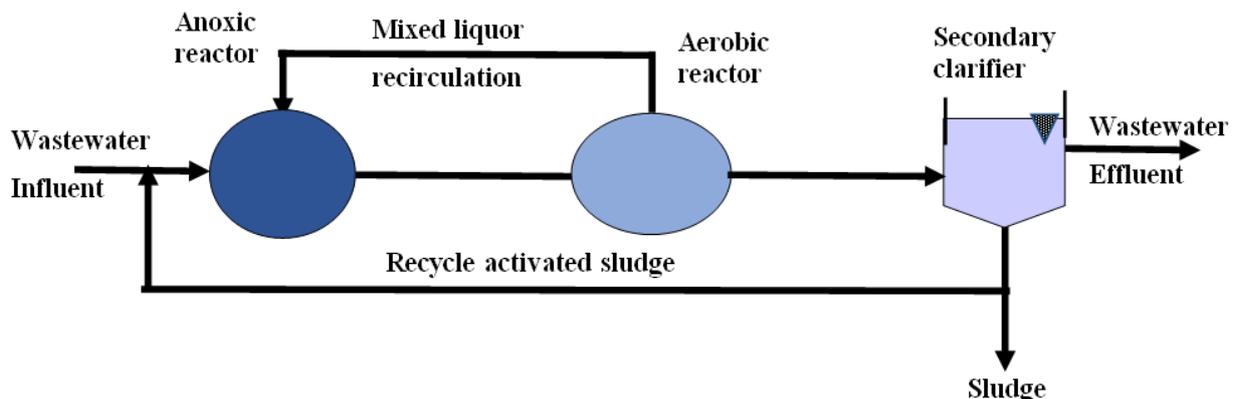


Figure 5. Nitrification process [5]

Methanol (CH₃OH) is commonly used as supplemental carbon source because the following reasons:

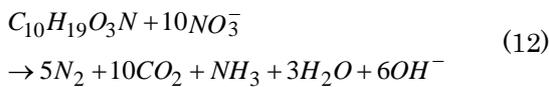
- i. it is inexpensive
- ii. it has a unique single - carbon compound structure
- iii. it supports growth of a specific bacterial population

ANAerobic AMMonia Oxidation (ANAMMOX) process is a denitrifying biological reaction in which autotrophic bacteria oxidize ammonia to nitrogen gas using nitrite as the electron acceptor [31]. Under anoxic conditions, the bacteria oxidized ammonia with the reduction of nitrite to produce nitrogen gas.

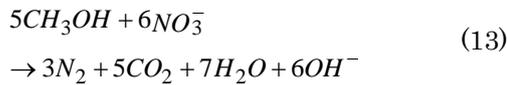
5.2.3.2. Denitrification Reactions and Stoichiometry

The different electron donors are methanol, ethanol and acetate.

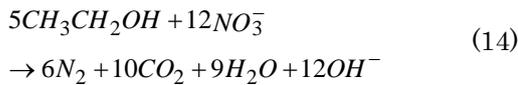
Biodegradable organic matter in waste water (C₁₀H₁₉O₃N)



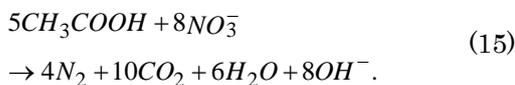
Methanol



Ethanol



Acetate



From the above reactions, one equivalent of alkalinity (OH) is produced per one equivalent of nitrogen

$$\frac{1 \text{ eq alkalinity produced}}{1 \text{ eq NO}_3\text{-N}} \rightarrow 3.57 \frac{\text{g of alkalinity as CaCO}_3}{\text{g nitrate nitrogen reduced}} \quad (16)$$

Dinitrification

$$\rightarrow 3.57 \frac{\text{g of alkalinity as CaCO}_3 \text{ produced}}{\text{g NO}_3\text{-N reduced}} \quad (17)$$

5.3. Available Anoxic Treatment Technologies

Different designs of denitrification have been developed based on the type of electron donors.

5.3.1. Wuhrmann System

This is a single-sludge process and post-denitrification system created by Wuhrmann [5,30]. Nitrogen removal is accomplished in the activated sludge process by the addition of a mixed anoxic tank aerobic nitrification (Figure 6). This is a post denitrification system that did not utilize an internal mixed liquor recycle to obtain significant utilization of the influent biochemical oxygen demand (BOD) [5,30]. It is a self-generated electron donor system [5,30].

- i. It uses endogenously generated organics
- ii. Methanol is added to improve denitrification
- iii. All influent organics utilized in aerobic
- iv. The rate of denitrification is proportional to the rate of endogenous respiration in the mixed liquor.
- v. It required long detention time in the postanoxic tank to achieved high efficiency of nitrate-removal
- vi. Exogenous carbon source may be added
- vii. Higher operating cost due to purchase of methanol.

5.3.2. Ludzack-Ettinger System (LES)

This is a pre-denitrification (pre-anoxic) system in which the primary reactor is anoxic (Figure 7). The influent wastewater is fed into an anoxic reactor which is followed by an aerobic reactor. The Ludzack-Ettinger process depends on the nitrate in the returned recycle sludge from the aerobic zone [5,30].

- i. The influent organics are utilized in the primary anoxic reactor.
- ii. The NO₃⁻ formed in the aerobic zone is returned to the influence as recycled activated sludge to the anoxic zone
- iii. The rate of denitrification is limited by the recycled activated sludge ratio to the influence.

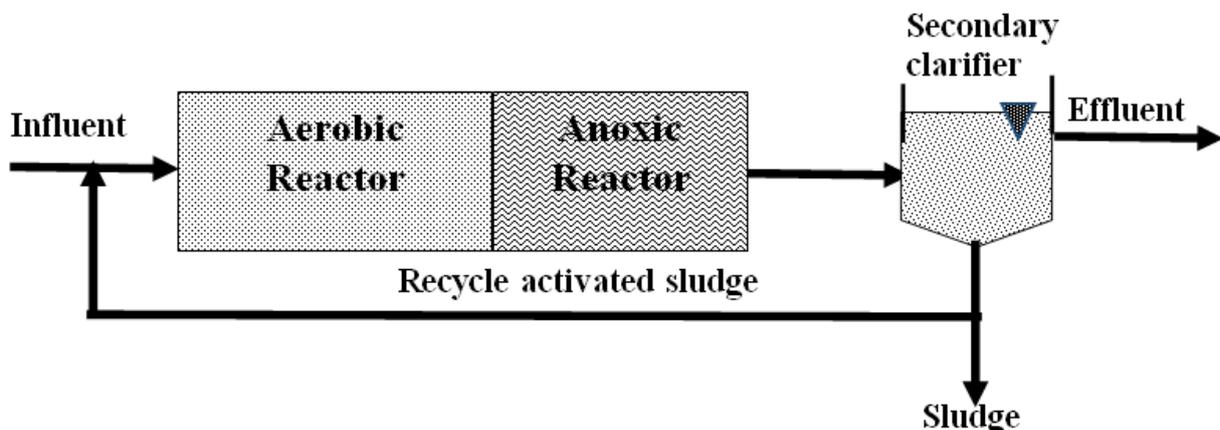


Figure 6. Wuhrmann single-sludge process and post-denitrification system [5,30]

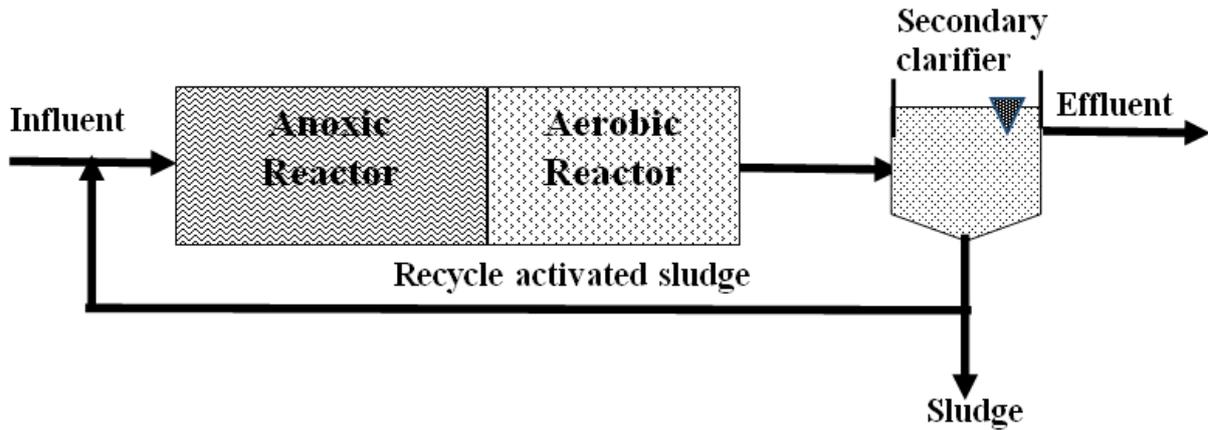


Figure 7. Ludzack-Ettinger System [5,30]

It has high nitrogen removal, however, the effluent NO_3 is greater than 4 mgN/l because the recycled sludge has upper limit of approximately 5:1 ratio [30].

5.3.3. Modified Ludzack-Ettinger (MLE)

The Modified Ludzack-Ettinger is one of the most commonly used biological nitrogen removal system. The original Ludzack-Ettinger design was modified by Barnard in 1973 by providing the internal recycle mixed liquor to feed more nitrate into the anoxic reactor directly from the aerobic reactor (Figure 8) [30]. There is an increase in the rate of denitrification and the overall nitrogen removal efficiency. The internal recycle flow ratio (IRFR) is determined as:

$$\text{IRFR} = \frac{q_r}{q_i} \tag{18}$$

Where q_r is the internal recycled flow rate, and q_i is the influent flow rate.

- i. IRFR typically ranged from 2 to 4 [30].
- ii. Requires a BOD/TKN ratio of 4:1 in the wastewater influent for effective nitrate reduction by pre-anoxic process.
- iii. Anoxic tank detention time is from 2 to 4 hours.
- iv. Can meet effluent standard of less than 10mg/l total nitrogen
- v. A total nitrogen concentration range of 4 to 7mg/l is achieved for treated domestic wastewater

The MLE can be used in existing activated sludge wastewater treatment facilities.

5.3.4. Bardenpho 4-Stage Process

This is a combination of pre-anoxic and post-anoxic system (Figure 9).

It was first developed in South Africa in the 1970s by Barnard and used in the United States in 1978 [30]. It consists of primary and secondary zones. The primary zone of the Bardenpho 4 stage is identical to the Modified Ludzack-Ettinger (MLE). The secondary anoxic zone provides denitrification for the unrecycled mixed liquor and nitrogen gas is released in the secondary re-aeration zone [30].

- i. Influent organics (BOD) are utilized in primary anoxic to provide carbon source.
 - ii. Complete denitrification is possible for low TKN/COD
 - iii. Methanol dosed increases denitrification rate as it provides carbon source for endogenous respiration.
 - iv. The concentration of dissolved oxygen (DO) in the secondary aerobic reactor is increased
 - v. Efficiency nitrogen removal in effluent is less than 3mg/L
 - vi. Large reactor volumes are required as bulk sludge is produced
- Biological phosphorus is also removed alongside nitrogen removal, hence the name Bardenpho.

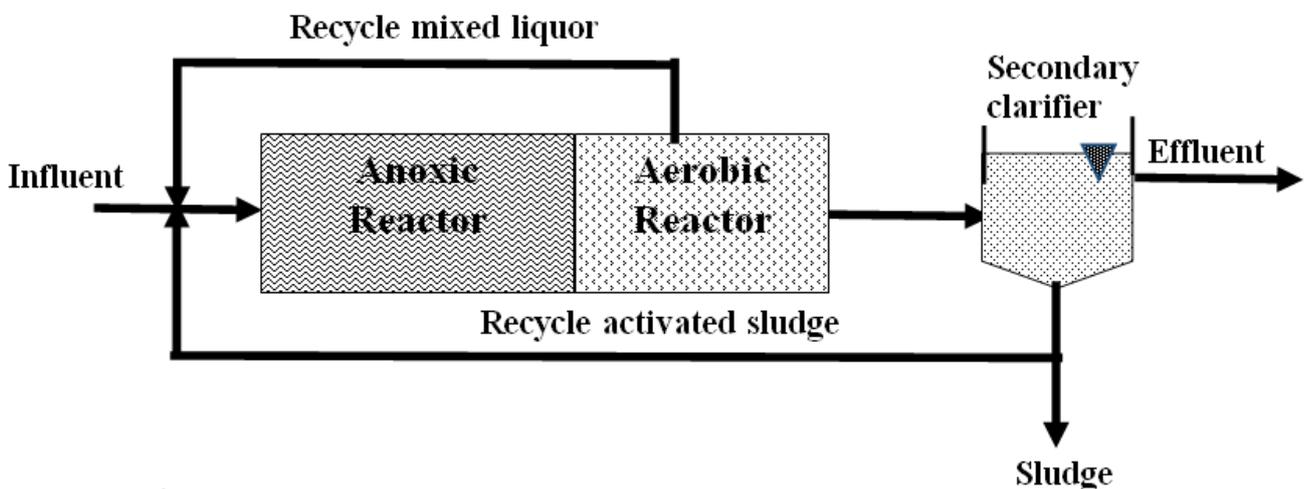


Figure 8. Modified Ludzack-Ettinger [5,30]

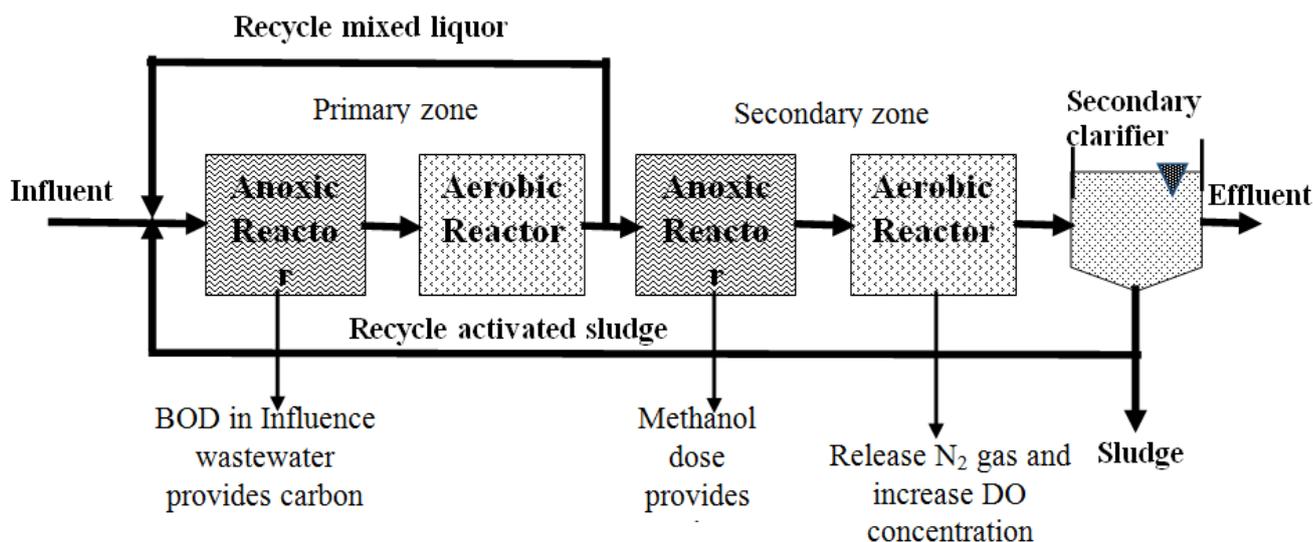


Figure 9. Bardenpho 4-stage process [5,30]

a. Advantages of Biological Denitrification

- i. Reduction in nitrogen concentration in wastewater effluent
- ii. Reduction in sludge in the secondary sedimentation tank. (SST)
- iii. Reduction in oxygen demand
- iv. Alkalinity (as CaCO_3) is recovered
- v. Higher reactor pH
- vi. Reduced attack to concrete

b. Disadvantages

- i. Requires pumps for mixed liquor recycle
- ii. Slightly more complex system
- iii. Requires larger reactor volumes
- iv. Will require longer sludge age to ensure nitrification

6. Conclusion

Generated wastewater effluents discharged into watercourses in Nigeria contained high concentrations of nitrogen and phosphorus which significantly exceeded stipulated maximum permissible effluent discharge standards. These nutrients cause eutrophication effect and deteriorate the quality of the receiving water bodies. To avoid excessive growth of algae and water hyacinths in watercourses in Nigeria, anoxic treatment of wastewater effluents for nitrogen and phosphorus removal is necessary. A combination of treatment technologies are available for nitrogen and phosphorus removal from wastewater. The application of both chemical and biological treatment can reduce concentrations of nitrogen and phosphorus in wastewater effluents to acceptable levels.

Competing Interests

Authors have declared that no competing interests exist.

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