

# NUTRIENT OPTIMIZATION FOR PULP & PAPER WASTEWATER TREATMENT PLANTS – AN OPPORTUNITY FOR MAJOR COST SAVINGS

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## ABSTRACT

Pulp & paper wastewater treatment plants (WWTP) often add nitrogen and phosphorus to ensure optimum performance. If there are insufficient nutrients for bacterial metabolism, an increase in effluent total suspended solids (TSS), biological oxygen demand (BOD) and/or chemical oxygen demand (COD) may occur. As well, nutrient deficiency can cause or contribute to acute or chronic regulatory toxicity. Nitrogen and phosphorus are a major cost for many wastewater treatment plants and represents a major opportunity for cost reduction.

Nutrient over addition commonly occurs but is not often recognized. Nitrogen over addition and subsequent nitrification and denitrification can significantly increase costs. It can also contribute to or cause process upsets manifested by severe biological reactor foaming, secondary clarifier scum and/or higher final effluent BOD and TSS discharges. Phosphorus over addition will not cause a process upset but increases operating costs and contributes to eutrophication.

Heterotrophic bacteria require nitrogen to metabolize BOD although over addition can result in the growth of unwanted nitrifying bacteria. The nitrifying bacteria consume considerable amounts of oxygen. For 1 mg of ammonia oxidized there is 4.6 mg/L of oxygen consumed. Nitrifying bacteria consume excess ammonia nitrogen (NH<sub>3</sub>-N) producing nitrite (NO<sub>2</sub>) and nitrate (NO<sub>3</sub>). In theory, reactor nitrate residuals should be stable if the reactor is not anoxic. When nitrate residuals are elevated secondary clarifier denitrification may occur. With this type of denitrification secondary clarifier sludge blanket can rise to the surface.

Extensive field experience utilizing newer wastewater assessment tools indicates denitrification can occur within the biological reactors of most pulp & paper WWTPs. With biological reactor nitrification and denitrification ammonia nitrogen residuals can be relatively low and nitrate not detectable. Subsequently this frequently results in nitrogen over addition.

The over addition and subsequent reactor nitrification and denitrification may not cause obvious process difficulties but can occasionally cause severe upsets.

It is estimated the previously unrecognized reactor denitrification is conservatively costing the pulp & paper

industry millions of dollars per year as a result of wasted nitrogen, power, defoamer and polymer costs.

The paper reviews mechanisms and conditions responsible for pulp & paper nitrification, denitrification and nutrient deficiency as well as related evaluation methods.

## Keywords

Nitrification, denitrification, nutrient deficiency, respirometer, specific oxygen uptake, ammonia, nitrogen, nitrate, phosphorus, pulp and paper, wastewater, fluorescence in situ hybridization

## INTRODUCTION

WWTP bacteria require nutrients to maximize BOD metabolism. The major nutrients required for bacterial growth are C, H, O, N, P and S. There are also micro nutrients needed that include Mg, K, Fe, Na, Ca, Mn, Zn, Cu, Mo as well as other nutrients (Gostick, 1990). Typically pulp & paper WWTPs are nutrient limited and only nitrogen and phosphorus chemicals are added. An upset can develop if there is a deficiency of nitrogen and/or phosphorus. Nutrient deficiency has the potential to increase TSS, BOD and/or COD losses. As well, nutrient deficiency can also cause regulatory acute and/or chronic toxicity.

All pulp & paper WWTPs require nitrogen and phosphorus for optimal treatment. Theoretically, for each 100 mg/L of BOD the bacteria require 5 mg/L of nitrogen and 1 mg/L of phosphorus. This is referred to as a BOD:N:P ratio of 100:5:1. In aerated lagoons the ratio is often referenced lower at about 100:2.5:0.5 due to biofeedback of nutrients from benthic sludge (Foster et al., 2003).

Nutrient requirements vary significantly between WWTPs due to operating condition dynamics, type of treatment and plant design. For these reasons it can be challenging with significant potential for upsets when nutrients are added based upon an BOD:N:P ratio.

The required nutrients are provided through nutrient addition, mill process and/or possibly from nitrogen fixation (Slade et al., 2004).

Faster rates of bacterial decay will lower nutrient requirements. Major factors influencing bacterial decay are sludge age and temperature with higher values lowering nutrient requirements (Jenkins et al., 2004).

Generally high rate (low sludge age) activated sludge plants require more nutrients than low rate (high sludge age) plants. Aerated lagoons have lower nutrient needs due to anaerobic decomposition of benthic sludge. If the released nutrients are available to aerobic bacteria, where BOD metabolism occurs, nutrient requirements will be low.

The nutrient addition rate is often based upon nutrient residuals after the first cell of treatment. Ammonia nitrogen (NH<sub>3</sub>-N) and ortho-phosphate residuals of 0.5 to 1 mg/L are typically recommended but many plants operate successfully in the 0.3 to 0.5 mg/L range (Foster et al. 2003). Target levels should be

site specific as significant over addition or deficiency can occur.

## NUTRIENT OPTIMIZATION

Ammonia nitrogen and ortho-phosphate target residuals of 0.5 to 1 mg/L prevents nutrient deficiency from occurring in most plants. Nutrient deficiency can develop when there is insufficient nitrogen and or phosphorus available for BOD metabolism. A deficiency can cause higher TSS, BOD and acute or chronic regulatory toxicity. Operating at higher target residuals minimizes the risk of nutrient deficiency but also increases operating costs, receiving water eutrophication and potentially can cause ammonia related process upsets.

Nitrogen and phosphorus is required for the growth of BOD consuming heterotrophic bacteria. These bacteria need nitrogen as ammonia nitrogen (NH<sub>3</sub> N) or nitrate (NO<sub>3</sub>) as well as phosphorus to maximize BOD removal efficiency.

If nitrogen addition is greater than heterotrophic bacteria requirements nitrification can occur. Nitrification is the biological oxidation of ammonia to nitrite and nitrate. There are two classes of nitrifying bacteria that include ammonia and nitrite oxidizers. The ammonia oxidizers convert ammonia to nitrite (NO<sub>2</sub>) and nitrite oxidizers convert nitrite to nitrate. The nitrifying bacteria grow relatively slowly compared to heterotrophic bacteria (Wagner et al., 2002). Under optimum conditions heterotrophic bacteria reproduce within 30 minutes while nitrifying bacteria multiple every 8 to 20 hours depending upon the type of bacteria. Due to the faster heterotrophic growth rate they “out compete” nitrifiers for ammonia nitrogen. When nitrogen is added in excess to the heterotrophic bacteria requirements nitrification typically occurs.

Nitrification can occur over a wide range of pH, temperature and sludge age conditions and are therefore not limiting factors for most plants. As a result nitrification occurs readily in most aerated lagoons and activated sludge plants. Even high rate activated sludge plants such as oxygen activated sludge systems will nitrify although sludge age may be relatively low. Even though nitrification frequently occurs it often cannot be identified without specialized assessment methods.

Denitrification is the breakdown of nitrate to nitrogen gas by denitrifying bacteria. Textbook denitrification occurs within secondary clarifiers or quiescent zones. The released nitrogen gas causes sludge to rise from the bottom to the surface when anoxic conditions exist (Jenkins et al., 2003).

Based upon field experience utilizing nitrifying bacteria fluorescence *in situ* hybridization (FISH) commercial probes and other nitrification and denitrification respirometry identification methods, biological reactor denitrification frequently occurs. Prior to the development of these methods it had been assumed reactor denitrification was not possible due to positive reactor D.O. residuals. Based upon field experience using FISH probes reactor nitrification and denitrification commonly occurs in many pulp and paper WWTPs (Kenny, 2003).

Although not previously recognized in pulp & paper WWTPs there are aerobic and facultative denitrifying bacteria that can exist in aerobic biological reactors. Aerobic denitrifying bacteria such as *Paracoccus denitrificans* have been identified by FISH probes. These denitrifying bacteria can use nitrate or oxygen as electron acceptors without a time delay for mobilization of the nitrate enzymes (Austin et al.).

With reactor denitrification a percentage of the released nitrogen remains within the floc. When these bacteria enter the secondary clarifier or quiescent zone a fraction can float immediately upon entry. This sludge eventually settles as the nitrogen gas dissipates over time.

For some WWTPs nitrate residuals can be an important indicator of nitrification and a valuable control tool. When nitrification is identified by significant nitrate residuals denitrification can be readily identified and controlled. If residuals are measured nitrogen addition can be based upon ammonia and nitrate residuals. With reactor denitrification nitrate residuals are often not detectable. As a result nitrification (& potential for denitrification) may not be recognized.

With reactor nitrification/denitrification nitrification likely occurs at the floc perimeter and denitrification within the floc. The liquid bulk D.O. residuals can be greater than 1 mg/L but within the floc residuals may be zero if oxygen transfer rates are too low.

Reactor nitrification and denitrification is not always obvious as it may not significantly hinder WWTP operations. Occasionally upsets develop with the cause difficult to determine as nitrate residuals are not detected. Operating personnel may incorrectly assume nitrification is not possible due to zero nitrate residuals.

In severe cases of reactor denitrification symptoms can include secondary clarifier floating sludge, sludge floating immediately upon sample collection and moderate to severe foaming. The foam is unique as it is dark and unusually viscous. The viscous foam is caused by nitrogen gas carrying bacteria to the surface where it becomes incorporated into the foam.

In less severe cases of reactor denitrification a thin layer of sludge may be observed at the clarifier surface with little or no foaming observed.

As well, nitrogen gas bubbles attached to the floc can be responsible for higher settle volume indexes (SVI). When filament bulking or nutrient deficiency cannot account for elevated SVIs it may relate to reactor denitrification.

Biological reactor nitrification/denitrification is difficult to troubleshoot and control due to the low ammonia nitrogen and nitrate residuals.

Nitrogen over addition is not often apparent as reactor denitrification masks the over addition. Under these

circumstances plant personnel may incorrectly determine nutrient deficiency is occurring.

Anecdotal aerated lagoon field experience indicates nitrogen feed rate doubling or tripling does not cause a significant increase in ammonia nitrogen or nitrate residuals. The additional ammonia is shunted into the reactor nitrification and denitrification cycle and therefore its effects are not apparent.

Adding nitrogen in excess of heterotrophic bacteria requirements has the potential to trigger an operational upset with the severity related to the food to microbiological mass ( $f/m$ ) ratio. At higher  $f/m$  the bacterial growth rates are greater resulting in decreased oxygen penetration to the centre of the floc. Under these conditions denitrification may occur within the floc.

This mechanism is similar to that responsible for the growth of type 1701 and *Sphaerotilus natans* filaments. Growth of these filaments is favoured when the food to microbiological mass ( $f/m$ ) ratio is high and dissolved oxygen level is low (Jenkins et al., 2003). The dissolved oxygen at the floc centre may approach zero even though the bulk D.O. can be relatively elevated. These filaments grow extending from the floc surface where the oxygen concentrations are higher. Similar conditions responsible for type 1701 and *Sphaerotilus natans* filament growth can also explain reactor denitrification.

WWTPs may operate for extended periods without experiencing an upset due to reactor denitrification. The exact trigger conditions responsible for such an upset is not fully understood but likely relate to higher mill BOD loading and/or sludge accumulation within the biological reactor. These sludge deposits are significant reservoirs for ammonia nitrogen and organic acids that can transfer upwards into the aerobic layer by means of diffusion (Slade et al., 2004). As the quantity of sludge increase, more ammonia is released causing further nitrification. Based upon field work, ammonia nitrogen within the sludge deposits can range between 20 and 500 mg/L. This nitrogen can be available to heterotrophic bacteria for BOD metabolism or to nitrifying bacteria for nitrification.

Organic acids migrating from sludge deposits have the potential to increase the  $f/m$  ratio, maximize heterotrophic bacterial growth (e.g. *zoogloal* bacteria) and decrease the D.O. within the biological floc. The rate of organic acid as well as ammonia nitrogen release is likely variable depending upon whether sludge upwelling is occurring. Subsequently this would affect nitrification as well as reactor denitrification.

When confirmed reactor denitrification can be controlled by decreasing nitrogen feed rates and if applicable by eliminating problem sludge deposits.

Where reactor nitrification and denitrification is suspect, technical confirmation is required. This can be accomplished utilizing FISH probes or respirometer evaluation methods. Prior to the development of these procedures reactor denitrification was very difficult to diagnosis or control.

Nutrient optimization without appropriate methods creates difficulty as it becomes challenging distinguishing between nitrification/denitrification and nutrient deficiency.

A number of aerated lagoon and activated sludge plants have successfully reduced or eliminated nitrogen and phosphorus addition. Although nutrients are not added they are obtained from mill sources and/or nutrients originating from sludge deposits.

WWTPs considering nutrient optimization should conduct an operations assessment with a focus on nutrient management. A nutrient reduction program can include anthrone polysaccharide, ammonia nitrogen/nitrate/ortho phosphate, microbiological and nitrification-nutrient deficiency laboratory and in-situ respirometry testing. As well some plants may consider FISH probe testing nitrifying and denitrifying bacteria.

There are filamentous bacteria such as *Thiothrix* spp., Type 021N that can grow at low nitrogen conditions and *Sphaerotilus natans*, *Haliscomenobacter hydrossis* and *Nostocida Limicola* 111 that may grow in low phosphorus conditions (Jenkins et al.). These filaments have other growth causes unrelated to nutrient deficiency and are therefore not reliable indicators of nutrient deficiency.

Anthrone polysaccharide testing is important to establish whether nutrient deficiency exists. The anthrone polysaccharide test is a chemical procedure to measure the bacterial polysaccharide content. High amounts of carbohydrates occur when the plant is nutrient limited. An anthrone polysaccharide content of less than 25% is normal and an indication that nutrients are not deficient (Jenkins et al., 2004). A normal polysaccharide level indicates nutrient addition is balanced or over addition may be occurring.

Sample preparation for aerated lagoons can present challenges due to low lagoon bacterial concentrations. Lagoons often operate between 100 and 200 mg/L of TSS. The anthrone polysaccharide test requires a TSS concentration of 2,000 mg/L or higher. Aerated lagoons can determine polysaccharide concentrations by centrifuging samples. Centrifuging is required as a significant fraction of the biological TSS may not readily be captured by gravity settling (Kenny et al. 2000).

Anthrone polysaccharide testing can determine whether there is a deficiency of nitrogen or phosphorus but cannot be used to assess the degree of nitrogen over addition. Determination of nitrification can be accomplished through microbiological techniques or with specialized respirometry procedures. If nitrification is confirmed and there are no measurable reactor nitrate residuals, it can be assumed biological reactor nitrification and denitrification is occurring.

If nitrifying bacteria are identified it is assumed nitrification is occurring. Nitrifying bacteria can be determined by morphological phase contrast microscopic identification or by FISH probe testing. Microscopic identification has its limitations as only two of ten or more nitrifying bacteria can be

identified based upon morphology. *Nitrosomonas* and *Nitrobacter* nitrifying bacteria are the only nitrifiers identifiable based upon morphology. If they are not observed, it cannot be assumed nitrification is not occurring as other nitrifiers may be present. Other nitrifying bacteria can be identified by plate culture or FISH commercial probe methods.

FISH commercial probe testing can be an important identification tool although there may be procedural limitations. As well, under reporting poses a potential concern due to bacterial slime that may limit probe penetration into the nitrifying bacteria.

Nitrification can also be determined with respirometry and ammonia recovery methods. In these procedures, a Strathtox respirometer measures the specific oxygen uptake rate (SOUR) of multiple samples controlled to the reactor temperature. The SOURs can be determined as follows:

1. Not inhibited control - 20 ml of endogenous wastewater + 1 ml of water.
2. Nitrifying inhibited control - A sample is prepared with a nitrifying inhibitor. 20 ml of the inhibited sample + 1 ml of water
3. Nitrification/Denitrification - 20 ml of endogenous wastewater + 1 ml of a known ammonium chloride solution.
4. Nitrification Inhibitor – A sample is prepared with a nitrifying inhibitor. Twenty ml of the inhibited sample + 1 ml of the known ammonium chloride solution are added to the tube.

The above tests are conducted for a specific time period or until the dissolved oxygen is depleted. The D.O. values are outputted to a computer with results graphically displayed. At test completion, the samples are filtered and ammonia nitrogen residuals determined for ammonia spiked and control samples. If the nitrification/denitrification + NH<sub>3</sub>-N sample has a significantly higher SOUR than the control, nitrification or nutrient deficiency could be occurring. If the wastewater is endogenous with low soluble BODs (e.g. < 10 mg/L) and the SOURs are significantly higher than the control sample, it can be concluded nitrification is occurring. As well, if the ammonia recovery test indicates significant ammonia consumption, this can provide additional verification of nitrification.

The purpose of the nitrification inhibitor is to provide an alternative verification method. If nitrifiers are present the inhibitor should partially or completely inhibit the nitrifiers. When ammonia nitrogen is added to the inhibited sample oxygen uptake rates should be similar to the non inhibited control SOURs. As well, complete recovery of the ammonia nitrogen should be possible.

The purpose of the nitrifying bacteria inhibited control is to determine if the inhibitor is impairing the uptake rate of the heterotrophic bacteria.

A similar procedure is used to determine if the wastewater is phosphorus deficient. A known phosphorus standard is added to a Strathtox tube containing endogenous wastewater. An equal volume of water is added to a second endogenous wastewater sample that acts as the control. At test completion the Strathtox program calculates the SOURs, samples are filtered and ortho-phosphate tests conducted. If there is a significant difference in the SOURs and/or ortho-phosphate consumption, phosphorus deficiency can be occurring.

The procedure can assist WWTPs with regulatory phosphorus limits to assess whether operating phosphorus residuals are adequate. Plants with strict limits may be required to maintain ortho-phosphate residuals approaching zero to comply with regulations. This testing can be an important tool in determining whether lower phosphorus residuals are optimal. For example, if there is no difference in the control and spiked SOURs and the bacteria have not consumed spiked phosphorus it could be concluded the ortho-phosphate residuals are adequate and the phosphorus addition rate can be maintained or possibly reduced.

This method in conjunction with anthrone polysaccharide testing can assist in reducing phosphorus costs. Although polysaccharide levels may be normal, phosphorus over addition can occur. By conducting phosphorus SOUR/phosphorus recovery testing information can be obtained to assist in decreasing phosphorus addition.

WWTPs reducing nutrients can also utilize soluble BOD and/or discharge SOURs as an additional tool to assess nutrient deficiency.

In complete mix systems soluble BODs can be used to assist with an assessment of nutrient deficiency. Observation of lower BOD removal efficiency and higher BODs can indicate nutrient deficiency if oxygen is not limited and/or no significant influent toxicity exists. As well, elevated BODs can relate to elevated sample TSS or incomplete biological treatment.

Higher sample TSS may increase the total BOD. To determine if the BOD is elevated due to the presence of bacteria soluble BOD testing is required. If the soluble BOD is elevated it may relate to nutrient deficiency. Soluble BOD testing has WWTP optimization limitations due to the five day delay in obtaining results.

Laboratory SOURs can theoretically provide similar information but inaccuracies exist as the lab testing does not reflect actual reactor conditions.

An alternative SOUR tool is the Strathkelvin Bioscope in-situ respirometer. The Bioscope is a field respirometer consisting of a sectioned four meter pole with a D.O. probe enclosed within a sampling container. The probe is inserted into the wastewater and when D.O. stabilizes the sampling chamber is closed. The oxygen depletion is measured and results graphically displayed on a computer panel. At test completion the mixed liquor suspended solids (mlss) or the mixed liquor

volatile suspended solid (mlvss) is inputted and an SOUR result calculated. A test is normally completed within 5 minutes.

Bioscope SOURs conducted prior to and after nutrient adjustment can provide critical nutrient optimization data. Lower SOURs indicate bacteria are maximizing BOD removal while higher SOURs indicate possible nutrient deficiency.

In-situ SOUR respirometer testing provides rapid and accurate data not obtained by other methods. With in-situ testing there is no error related to delay between sampling and testing, temperature or the test D.O. start point. In laboratory SOUR testing the sample is saturated with oxygen and D.O. readings are recorded after about 30 seconds. The decision regarding the D.O. start point introduces significant error.

With in-situ respirometry this inaccuracy is eliminated as the test commences when the D.O. stabilizes. With in-situ testing the start point is the actual reactor D.O. residual. For example if the reactor D.O. is 2 mg/L then the Bioscope test starts at this value. In laboratory SOUR testing the start point would normally be at a much higher value. This technological advancement allows personnel to obtain real time data that can assist with nutrient addition adjustments.

## CONCLUSION

Nutrient management can be improved for many WWTPs with substantial cost savings possible. Inter relationships between nutrients and the wastewater bacterial growth environment can be complex requiring specialized knowledge that surpasses traditional nutrient residual monitoring and control.

Many pulp & paper aerated lagoon and activated sludge plants over add nutrients as they are unaware of reactor nitrification and denitrification or of lower phosphorus requirements. As well, WWTPs decreasing nutrient addition may also encounter nutrient deficiency without adequate nutrient optimization tools and knowledge.

There exist significant opportunities to optimize WWTP operations through new nutrient assessment methods and technology. Nutrients requirements are site specific with nutrient assessments important in determining potential cost savings for individual plants.

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