Technical Publication

Title: On-Line Monitoring of Nitrification Processes Using ChemScan Process Analyzers

ASA Publication Number: 35

Presented at: Biotronics Technologies, Inc.
White Paper

On-Line Monitoring of Nitrification

Processes Using ChemScan™ Process Analyzers

Published for:

Biotronics Technologies, Inc.
W226 N555B Eastmound Drive
Waukesha, WI 53186
(414) 896-2650 ext. 136

by:

ENVIRONMENTAL / HEALTH SERVICES
Ken Neu
P.O. Box 21
Richfield, WI 53076
(414) 628-1367

May 31, 1994

Abstract

The nitrification reaction that takes place at wastewater treatment plants (WWTPs) is a two-step process carried out by two separate microorganisms. Dissolved oxygen level in the water has served as the primary indicator that the microorganisms have sufficient oxygen to function and that the reaction is proceeding properly.

An on-line, real-time, reagentless monitoring device has been developed, partly funded by NASA research, that is capable of accurately differentiating between and measuring nitrate-nitrogen (NO_3-N) and nitrite-nitrogen (NO_2-N) in water and wastewater streams. This device, the ChemScan™ on-line process analyzer, is able to instantaneously measure the amount of NO_2-N produced during the first step of the nitrification process. The analyzer can also monitor the second-step conversion of NO_2-N to NO_3-N. Used in combination with dissolved oxygen and pH probes, the ChemScan™ process analyzer can be used to provide automated control of the nitrification reaction process in WWTPs, resulting in greater efficiency and cost savings.

I. Introduction

During the past 10 years, many research reports, technical papers and publications have discussed the ammonia, nitrite and nitrate reaction kinetics in some detail (Brennen and Argaman, 1990; Hanaki, et al., 1990; Sedlak, 1989; Manual of Practice, 1983; U.S. EPA, 1993). However, few of the papers have placed great emphasis on the monitoring of nitrite concentration as part of the nitrification process control strategy. This may in part be due to the lack of instrumentation for the rapid, on-line measurement of nitrite. However, as this technology is now available, nitrite and nitrate concentration monitoring should be considered for inclusion in process control strategies.

This new ability to respond rapidly to changes in the nitrification process at WWTPs using ChemScan™ measurements should result in operation and maintenance savings. The on-line ChemScan™ process analyzer registers process chemistry changes instantaneously and, through the use of automated blower and pump controls, can adjust oxygen delivery, return activated sludge (RAS) flow and sludge wasting rates. This real-time, reagentless control strategy has the potential to reduce the frequency of manual laboratory process control testing and can reduce WWTP power costs by optimizing oxygen delivery and pumping during the entire 24-hour diurnal cycle. Automated adjustments could be made to the RAS rate or the mean cell residence time (MCRT) by changing the waste activated sludge (WAS) rate. In cases where flow equalization is used, this device could also be connected to the equalization tank controls.

The need for on-line nitrification process monitoring is great because the nitrification process is effected by biological mechanisms rather than simple chemical reactions. Therefore the rate of the various stages of the reaction can be affected by the non-optimization of any one of several parameters, rapidly putting the process into non-compliance. Some of the factors that affect nitrification are listed in Table 1.

| Table 1. |
|---|
| Factors Affecting Nitrification |
| - Temperature |
| - pH and alkalinity relationships |
| - MCRT/WAS rate, RAS rate |
| - Bulk dissolved oxygen concentration |
| - Heterotroph/nitrifier competition |
| - Nitrosomonas to Nitrobacter ratio |
| - Substrate composition variation, electron donor substrate concentration |
| - Half saturation coefficient in relationship to mass transport limitations and diffusional resistances |
| - Multi-substrate limiting kinetics that may affect the relative oxygen uptake rate under transient conditions and varying floc sizes |
| - Toxic substance concentrations, including free ammonia, or free nitrous acid or nitrite buildup. |

With the current technology, when WWTP nitrification efficiency rate is reduced, the operations staff may take a long time to recognize the need for process changes and respond with manual adjustments such as an increase in the oxygen supply, the hydraulic retention time, the RAS rate or the sludge age (by decreasing the wasted sludge rate). In many cases, operator response time is slow because laboratory tests for process control purposes take time and are manpower intensive. Although field test kits are less costly and time consuming than laboratory tests, they still require sample collection and manpower to conduct the tests. Many times operators rely on sensory perception alone to operate the plants, only to find out several days later that the plant has been in non-compliance with effluent permit requirements. Real-time process chemistry analysis would lead to safer, more cost-effective plant operation. Bundgaard, et al. (1993), studied five biological nutrient removal (BNR) plants that were using on-line measurements and concluded that on-line control strategies reduced consumption of both energy and chemicals and improved the effluent quality at the plants.

II. Nitrite Measurement as the Key Control Parameter

Although dissolved oxygen has historically been the main process control parameter, the effects of other limiting factors that may show up earlier can now be monitored. In some cases, an increasing level of nitrite may be used as a first indication of a low dissolved oxygen concentration, which may become inhibitory to the Nitrobacter organisms. However, with emphasis placed on increased plant efficiency and BNR (where a low D.O. zone is essential for some processes), there are more parameters than dissolved oxygen that become important. As effluent permits become more restrictive, a greater understanding of the biological mechanisms and process conditions to achieve lower effluent values becomes necessary, specifically in terms of nutrient reduction.

<u>Nitrogen Conversion Kinetics</u>

The nitrification of ammonia is a two-step process. The first step, conversion of ammonium to nitrite, is mediated by <u>Nitrosomonas</u>. The second step, conversion of nitrite to nitrate, is mediated by <u>Nitrobacter</u> microorganisms. Oxygen is essential to both steps. The equations below demonstrate this two-step conversion of ammonia to nitrate (U.S. EPA, 1993):

$$NH_4^+ + 3/2\ O_2 \longrightarrow 2H^+ + H_2O + NO_2^-$$

$$NO_2^- + 1/2\ O_2 \longrightarrow NO_3^+$$
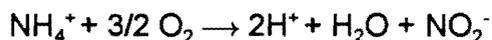
(The ammonium ion NH_4^+ is in a pH dependent equilibrium with ammonia and hydrogen ion: $NH_4^+ \rightleftharpoons NH_3^- + H^+$ [Sawyer and McCarty, 1978].)

Benefield and Randall (1980) illustrate the nitrogen conversion reaction in a polluted stream in Figure 1. This figure can also be used to represent nitrate/nitrite levels within a wastewater treatment plant. The organic nitrogen (@ approx. 32 mg/L) would include proportionately about 20-22 mg/L of NH_3-N, given the general composition of domestic sewage. Upon initial nitrification, the NO_2-N concentration could peak at up to 5 mg/L or more. As NO_2-N oxidation to NO_3-N takes place, the NO_2-N concentration would be reduced to levels below 1.0 mg/L while the NO_3-N concentration would increase. In addition, as shown in formulas for nitrification reactions and equilibria (see equations below) by Anthonisen, et al. (1976), free ammonia and nitrous acid are also present during the reaction.
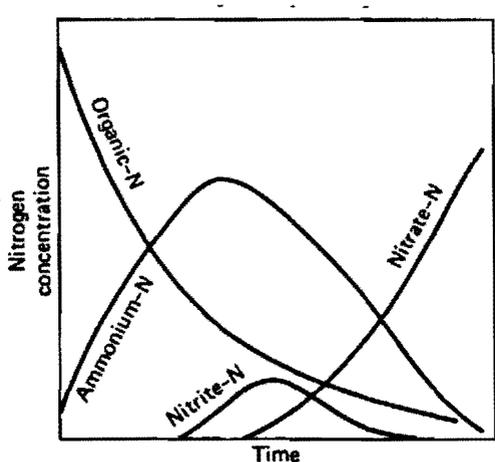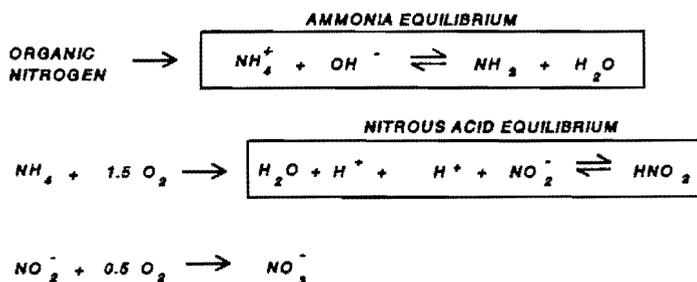

Figure 1. Nitrogen Conversion in a Polluted Stream. (After Sawyer and McCarty, 1967.)

AMMONIA EQUILIBRIUM

$$\text{ORGANIC NITROGEN} \longrightarrow \boxed{NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O}$$

NITROUS ACID EQUILIBRIUM

$$NH_4 + 1.5\ O_2 \longrightarrow \boxed{H_2O + H^+ + H^+ + NO_2^- \rightleftharpoons HNO_2}$$

$$NO_2^- + 0.5\ O_2 \longrightarrow NO_3^-$$

In a plant that usually nitrifies fully (<1.0 ppm ammonia-nitrogen [NH_3-N] remaining in the effluent), one of the first signs of a decrease in nitrification rate is usually a decrease in the NO_3-N concentration and an increase in the NH_3-N and NO_2-N concentrations. In shock organic load situations, a concentration-corresponding decrease in dissolved oxygen is usually noted as well. A reported 65-75% of the oxygen required for nitrification is used in the initial reaction from NH_3-N to NO_2-N.

4

Control Parameters

Historically, automation of process controls in the wastewater treatment industry has been slow in acceptance by design engineers and use by WWTP operators. Until approximately 10 years ago, technologies were basically not available for on-line automation in WWTPs. Manual operation by physical manipulation of motor/blowers and pump controls was the usual level of control provided to the operator.

The majority of the WWTPs in the U.S. were built prior to 1985, when automated process control was virtually non-existent. So, at a practical level, corrective action to maintain or to increase nitrification efficiency usually involves operator intervention to manually adjust oxygen supply, RAS and/or WAS rate or to change reaction time by manual adjustment of equalization tank flow.

Because dissolved oxygen is an important parameter to monitor during the biological treatment process, and given the state of technology until recently, the mode of operation was usually to provide a sufficiently high dissolved oxygen level to assure adequate biological oxygen demand (BOD) reduction.

However, some researchers have indicated that nitrite build-up is independent of oxygen concentration. Stenstrom and Song (1991) indicated that an optimal dissolved oxygen concentration to achieve nitrification while reducing aeration costs has not been established. These researchers attempted to explain the effects of oxygen transport on nitrification because to achieve efficient nitrification, a clearer quantification of the effects of dissolved oxygen concentration and the identification of other interdependent factors and their effects were needed. Stenstrom and Song developed a model, compared it with the Monod model and other models and described the reaction kinetics.

Among many conclusions reached by Stenstrom and Song, one is that under steady-state (laboratory) conditions the apparent limiting dissolved oxygen concentration for nitrification in the activated sludge process ranges from 0.5 mg/L to 2.5 mg/L, depending on MCRT (i.e., sludge age) and the degree of mass-transport resistance. They "recorded nitrite accumulation in a high dissolved oxygen (6-8 mg/L) steady-state (laboratory) reactor and concluded in part that the rate of NH_3-N oxidation by Nitrosomonas is typically the rate-limiting step under steady-state conditions, but the rate of NO_2-N oxidation under transient conditions appears to be correlated with transient increases in the rate of NO_2-N production rather than with low dissolved oxygen concentrations."

The above statement makes it clear that there could be parameters other than dissolved oxygen to adjust and control to optimize nitrification efficiency. The NO_2-N accumulation phenomenon appears to be a significant parameter to monitor for more rapid adjustment of process controls to optimize treatment.

The organism responsible for nitrite oxidation to nitrate, Nitrobacter, has been reported by some researchers (Alleman, 1984; Randall and Buth, 1984; U.S. EPA, 1984; Anthonisen, et al., 1976; Suthersan and Ganczarczyk, 1986; Pantea-Kiser, et al., 1990; Lazarova, et al., 1994) to be more sensitive (i.e., its metabolic processes are more easily affected negatively) than Nitrosomonas (ammonia -> nitrite) to changes in oxygen concentration, pH and toxics, even though Nitrobacter exhibits a more rapid metabolic rate under non-limiting conditions. That being the case, nitrite usually gets converted into nitrate quickly because of Nitrobacter's more rapid metabolic rate.

However, slight changes in dissolved oxygen or pH (or other parameters) may become limiting for <u>Nitrobacter</u> before they become limiting for <u>Nitrosomonas</u>. If <u>Nitrobacter</u> has insufficient oxygen or is inhibited in some other way, the nitrite - > nitrate kinetic conversion rate may decrease and nitrate concentration will decrease. Then, nitrite production continues but the nitrite is not converted to nitrate. Thus, the nitrite may build-up in some cases. Figures 2 and 3 show Anthonisen, et al. (1976), documentation of typical nitrogen transformations during non-inhibited and inhibited nitrification batch experiments. Alleman (1984) lists at least seven conditions under which an elevated nitrite concentration might be realized in a nitrification system, including reduced temperatures, limiting O_2 or CO_2 presence, elevated pH, free ammonia presence, elevated solids wastage, acute process loadings and cryptic nitrate reduction. Alleman also provided laboratory results of bench-scale nitrification studies to demonstrate that a nitrite or nitrate product <u>could be regulated</u> by manipulating certain of these conditions.

If the process is incorrectly monitored, nitrite (and possibly free NH_3, free nitrous acid or other substances) may build up to toxic concentrations or dissolved oxygen could drop to inhibition levels, all of which could create ammonia bleed-through. Some researchers (Anthonisen, et al., 1976; Suthersan and Ganczarczyk, 1986) estimate that nitrite, free ammonia, free nitrous acid, and other materials are up to 100 times more inhibitory to the metabolism of the microbes than the equivalent concentration of nitrate. Therefore, on-line, real-time NO_2-N observation is a key control parameter. ChemScan™ is the only technology available for real-time detection of NO_2-N and NO_3-N in wastewater.

Figure 2. Schematic of nitrogen transformations during noninhibited nitrification, batch experiment.

III. Simultaneous Nitrate and Nitrite Monitoring Strategy

A ChemScan™ on-line, real-time monitoring instrument can provide instantaneous NO_2-N <u>and</u> NO_3-N concentration readings simultaneously. In conjunction with dissolved oxygen concentration and pH data, an initial automated process control strategy can be developed. In a WWTP that is designed with total nitrification capability, actual in-plant data patterns should be generated, logged and interpreted. These concentration relationships would provide set-point concentration ranges of operation for each parameter of importance. This process control strategy would include, but not be limited to, in-plant manual or automated adjustments in process flow rate, air delivery, RAS rate or WAS rate. Critical
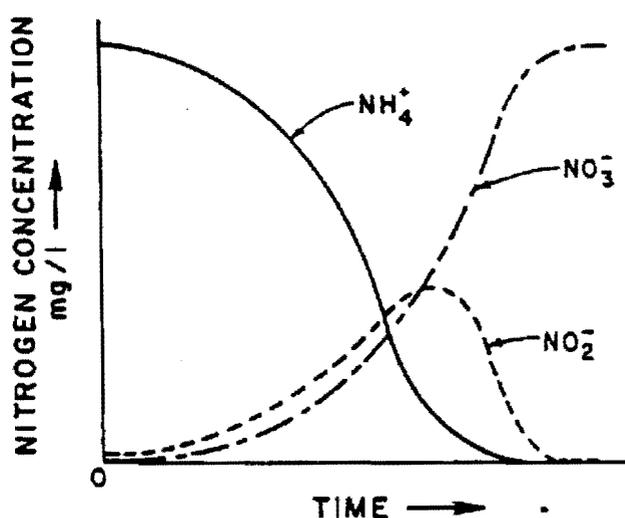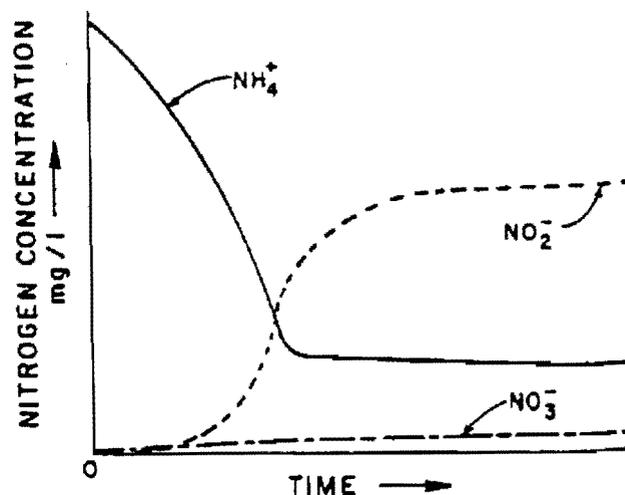

Figure 3. Schematic of nitrification with inhibition of nitrite oxidation, batch experiment.

6

parameter high and low set points (dissolved oxygen, NO_2-N, NO_3-N, pH) could also be used as signals to initiate further corrective action steps, should the process not come into line with normal or expected concentration ranges.

Chen and Lin (1993) have described denitrification in detail and show the NO_2-N and NO_3-N concentrations over time in several experiments. The new, on-line NO_2-N/NO_3-N monitoring system could be useful to monitor and optimize denitrification in a WWTP as well, once basic parameter concentration range set points have been defined. Suthersan and Ganczarczyk (1986) suggest that denitrification could proceed directly from nitrite and be more economical because reduced oxygen and energy requirements would result.

This control strategy could also save energy dollars. The system could be automated so that during low-flow or low-organic load periods the process air delivery could be automatically trimmed, based on satisfactory NO_2-N and NO_3-N results. Of course, occasional process monitoring of NH_3-N would still need to be conducted and compliance testing would need to be performed according to the National Pollution Discharge Elimination System (NPDES) permit schedule.

IV. Summary

The advent of the ChemScan™ on-line process analyzer, a device sensitive enough to accurately differentiate NO_2-N from NO_3-N instantaneously and repeatedly in an on-line wastewater treatment environment, could provide a dimension of nitrification process control not previously available. This tool could reduce potential permit violations and improve effluent quality and process efficiency. It would improve process operations and laboratory personnel awareness of the treatment process and process control strategies and in turn it would save energy, lower operation and maintenance costs due to overall energy, chemical and manpower cost reductions.

References

1. Alleman, J. E., 1984, "Elevated Nitrite Occurrence in Biological Wastewater Treatment Systems," Water Science and Technology, vol. 17, Amsterdam, IAWPRC, pp. 409-419.
2. Anthonisen, A. C., Loehr, R. C., Prakasam, T. B. S. and Srinath, E. G., 1976, "Inhibition of Nitrification by Ammonia and Nitrous Acid," WPCF Journal, vol. 48, no. 5, pp. 835-852.
3. Benefield, Larry D. and Randall, Clifford W., 1980, Biological Process Design for Wastewater Treatment, Prentice-Hall, Englewood Cliffs, New Jersey.
4. Brennen, A., Argaman, Y., 1990, "Effect of Feed Composition on Aerobic Volume Fraction and Recycle Rate on Nitrogen Removal in the Single-Sludge System," Water Res., vol. 24, no. 8, pp. 1041-1049.
5. Bundgaard, E., Onnerth, T. B. and Andersen, K. L., 1993, "Optimization of Biological Nutrient Removal Plants by On-Line Control," Proceedings of the Water Environment Federation, 66th Annual Conference and Exposition, vol. 3, Anaheim, California.
6. Chen, K. C. and Lin, Y. F., 1993, "The Relationship Between Denitrifying Bacteria and Methanogenic Bacteria in a Mixed Culture System of Acclimated Sludges," Water Res. vol. 27, no. 12, pp. 1749-1759.

7. Hanaki, K., Wanatawin, C. and S. Ohgaki, 1990, "Nitrification at Low Levels of Dissolved Oxygen with and without Organic Loading in a Suspended-Growth Reactor," Water Research, vol. 24, no. 3, pp. 297-302.
8. Lazarova, V., Capdeville, B. and Nikolov, L., 1994, "Influence of Seeding Conditions of Nitrite Accumulation in a Denitrifying Fluidized Bed Reactor," Water Research, vol. 28, no. 5, pp. 1189-1197, IAWQ, London, U.K.
9. Manual of Practice FD-7 Facilities Design, 1983, "Nutrient Control," Water Pollution Control Federation, Alexandria, Virginia.

Bibliography

1. Almeida, J. S., Julio, S. M., Reis, M.A.M. and Carondo, M. J. T., 1993, "Competition Between Nitrate and Nitrite Reduction in Pseudomonas fluorescens," Unv. Nova de Lisboa, Lab. Eng. Bioquimica, Mt. Caparica, Portugal.
2. American Society for Testing and Materials, 1976, "Standard Practice for Oxidation - Reduction Potential of Water," Designation: D 1498-76, ASTM, Philadelphia, Pennsylvania, pp. 184-190.
3. Antonie, R., L., 1976, Fixed Biological Surfaces - Wastewater Treatment, CRC Press, Cleveland, Ohio, p. 10.
4. Lauderlout, H. and Van Tichelen, L., 1960, "Kinetics of Nitrite Oxidation by Nitrobacter winogradski," J. Bacteriology, 79:39, pp. 39-42.
5. Masuda, S., Watanabe, Y. and Ishiguro, M., 1991, "Biomass Properties and Simultaneous Nitrification and Denitrification in Aerobic Rotating Biological Contractors," Water Science and Technology, 23(7/9), pp. 1355-1363.
6. McClintock, S. A., Randall, C. W. and Patterkine, V. M., 1991, "Effects of Temperature and Mean Cell Residence Time on Biological Nutrient Removal Process," Proceedings of the 64th Annual Water Pollution Control Conference, Toronto, Canada, pp. 1-16.
7. Morales, L. M., Lynch, D. P. and Daigger, G. T., 1991, "Cost Impacts of Upgrading Wastewater Treatment Plants to Provide Nutrient Removal," Proceedings of the 64th Annual Water Pollution Control Federation Conference, Toronto, Canada, pp. 1-9.
8. Munirathinam, K., and Stover, E. L., 1991, "Optimization of Biological Nutrient (N & P) Removal Using Three-Stage Anaerobic, Anoxic, and Aerobic Process," Proceedings of the 64th Annual Water Pollution Control Federation Conference, Toronto, Canada, pp. 1-10.
9. Neu, K. E., 1993, "Upgrading of Rotating Biological Contractor (RBC) Systems to Achieve Higher Effluent Quality, Including Biological Nutrient Enrichment and Reduction Techniques, "Proceedings of the 2nd International Conference on Upgrading of Wastewater Treatment Plants, Berlin, FRG, September, IAWQ, London.
10.Rusten, B., 1982, "Nitrogen Removal from Wastewater - Nitrification and Denitrification is a Rotating Biological Contractor Without External Carbon Source," Doctor of Engineering Thesis, Division of Hydraulic and Sanitary Engineering, University of Trondheim.
11.Sen, D., Randall, C. W., Grizzard, T. J. and Knocke, W. R., 1991, "Impact of Solids Handling Units on the Performance of Biological Phosphorous and Nitrogen Removal Systems," Proceedings of the 64th Annual Water Pollution Federation Conference, Toronto, Canada, pp. 1-9.
12.Data Summary: Denitrification Process Monitoring Demonstration Project. Hookers Point Advanced Waste Treatment Facility, Tampa, Florida. Biotromics Technologies, Inc., Waukesha, Wisconsin, June, 1993.
13.Watanabe, Y., Lee, C., Koike, M. and Ishiguro, M., 1990, "Nitrification Kinetics and Simultaneous Removal of Biomass and Phosphorus in Rotating Biological Contractors," Water Science and Technology, 22(314), pp. 169-178.

Tampa Florida AWT Facility

Denitrification Effluent

UV—6100 Ten Min Scans from Noon 5/2/93

—— Nitrate (NO3—N)   —— Nitrite (NO2—N)