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Ammonia Removal Options for High Purity Oxygen Activated Sludge Systems:

a Literature Review

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Introduction

The current National Pollutant Discharge Elimination System (NPDES) discharge permit for Plant A does not contain regulatory limitations for ammonia discharges into the receiving waters for the plant. However, it is anticipated that future permits might contain ammonia discharge requirements (*Redacted, 2008*). This literature review, in anticipation of potential discharge permit changes, was undertaken to investigate and identify ammonia removal treatment processes that can be incorporated with existing treatment processes at Plant A.

Nitrification, the biologically mediated oxidation of ammonia to nitrate, is generally accomplished in the biological secondary treatment process of facilities that are required to remove ammonia. The secondary treatment process is operated in a manner that facilitates development of a robust population of nitrifying microorganisms that oxidize ammonia simultaneously with other organisms that oxidize organic matter in the water. In tandem, these microbes produce an effluent low in BOD and ammonia.

At Plant A, biological, secondary treatment is accomplished using the UNOX, high purity oxygen activated sludge (HPOAS) process. The HPOAS process is characterized by covered oxidation tanks, use of high purity oxygen as a dissolved oxygen source, and short solids detention times (Gilligan, 1999). Some of the physical and operating characteristics of the HPOAS system limit options for incorporating ammonia removal into the secondary treatment process. The objective of this investigation is to identify ammonia removal processes compatible with the HPOAS system used by the Plant A.

Biological Treatment

Ammonia in wastewater results from the breakdown of proteins and amino acids in organic waste (Pressley et al., 1972). Conventional wastewater treatment does not remove ammonia and the ammonia that enters the plant is discharged to receiving waters with plant effluent. Ammonia exerts an oxygen demand in receiving waters, which can depress or deplete dissolved oxygen, impacting the aquatic ecosystem. Ammonia can also contribute to eutrophication and can be toxic to sensitive aquatic biota (Constantine, 2006; Ramisetty, 1999.). For these reasons, ammonia is regulated for wastewater discharges to nitrogen-sensitive receiving waters by limiting the allowable discharge of ammonia or total nitrogen. Wastewater treatment plants with ammonia or total nitrogen discharge limitations must incorporate treatment processes that remove those constituents as part of the wastewater treatment process.

Nitrification, carried out by aerobic, autotrophic bacteria *Nitrosomonas* and *Nitrobacter*, requires an aerobic environment and creates an oxygen demand above that required for oxidizing carbonaceous organic matter (cBOD). Nitrifying bacteria are much slower growing than organisms that consume cBOD. Therefore, incorporating nitrification into a suspended growth, secondary treatment process necessitates providing additional aeration capacity and significantly increasing the solids retention time to allow establishment of a robust population of nitrifying bacteria in the treatment process. Because of the long solids retention times required for nitrification, fixed film and extended aeration processes are effective nitrifying systems.

Wastewater treatment plants with conventional activated sludge secondary treatment processes can often incorporate nitrification into the treatment process, without modifying existing equipment, by making operational changes. Nitrification can be induced by increasing the sludge age, which gives the slower growing nitrifying bacteria time to develop a large, robust population. When nitrification starts, system oxygen demand increases, requiring an increase in the supplied volume of air to the activated sludge system. Nitrification consumes alkalinity and nitrifying systems can depress secondary effluent pH, which can inhibit nitrification. A sludge age of ten days or longer is required to establish and maintain an adequate population of nitrifiers to effect nitrification and the system pH must generally be maintained above 6.5 to avoid stressing the nitrifying bacteria. These requirements, relatively simple to achieve in a conventional activated sludge process, can be difficult to achieve in a HPOAS system.

HPOAS systems are designed to be operated with short mean cell residence times (MCRTs). At Plant A, the HPOAS system is operated at an average MCRT of about two days. Past attempts to increase the Plant A operating MCRT have resulted in significant sludge foaming and bulking problems caused by filamentous organism growth. Operating Plant A at MCRTs longer than about two days has not proven to be sustainable. Because nitrification requires an MCRT of ten days or longer, nitrification does not occur in the low MCRT environment of the Plant A HPOAS system.

Aerobic oxidation of organic matter in biological wastewater treatment produces carbon dioxide. In conventional dissolved air activated sludge processes, the carbon dioxide (CO_2) is released to the atmosphere. In the HPOAS process, with covered tanks, CO_2 accumulates in the headspace gas. The increased partial pressure of CO_2 causes the concentration of CO_2 dissolved in the mixed liquor to increase, depressing the mixed liquor pH. Many HPOAS processes operate in the pH range below 6.5. When pH approaches 6.0, nitrifying microbes become stressed and nitrification is inhibited. To compound this low pH problem, nitrification consumes alkalinity from the mixed liquor, which can further depress pH and further inhibit nitrification.

Newer designs for HPOAS systems have incorporated biological nutrient removal capability. About one in six of the 110 operating municipal HPOAS systems in North America is designed for BNR (Gilligan, 1999). HPOAS BNR process designs incorporate some uncovered tanks to vent carbon dioxide and additional reactor tanks for denitrification and biological phosphorus removal.

Nitrification in the HPOAS Process using Bioaugmentation

The short MCRT and low pH characteristics of the HPOAS process limit the ability of nitrifying organisms to grow. However, they do not limit the ability of a viable population of nitrifying organisms, introduced into the HPOAS environment, to effect nitrification. If nitrifying organisms are grown in a separate reactor and continuously fed to the HPOAS process, a process called bioaugmentation, nitrification will occur in the HPOAS reactor. In separate, full-scale studies, Neethling et al. (1998) and Randall and Cokgor (2001) reported successful nitrification in HPOAS processes using bioaugmentation. The bioaugmentation source for both projects was waste sludge from parallel, dissolved air activated sludge, nitrifying plants. In the Portland, Oregon study reported by Neethling et al., no operational changes were made to the HPOAS plant, other than the introduction of the waste sludge from the nitrifying plant. Within two weeks, nitrification in the HPOAS plant was producing effluent ammonia concentrations between 1 – 5 mg/L and after one month, effluent ammonia concentrations stabilized below 1 mg/L.

In the Richmond, Virginia study reported by Randall and Cokgar, a five-stage HPOAS UNOX process was converted to a BNR process for removing both phosphorus and total nitrogen. Modifications included converting the first stage to an anoxic/anaerobic stage for denitrification and phosphorus removal. The last stage was converted to diffused air aeration and the cover was removed to facilitate CO_2 removal and concomitant pH elevation. The modified process achieved 84% ammonia removal, 55% total nitrogen removal, and 74% total phosphorus removal. The authors reported that the HPOAS plant was derated from 30 mgd to 16 mgd to reliably achieve biological nutrient removal but did not specify which nutrient removal process necessitated the derating.

Nitrification of solids dewatering side streams can be a rich source of nitrifying bacteria for bioaugmenting the activated sludge treatment process (Carrio, 2003; Parker et al., 2007). Side stream liquors from solids treatment and dewatering processes are high in ammonia concentrations, contributing significantly to the total nitrogen load to a wastewater treatment plant. In wastewater treatment plants with sludge digestion, the return liquor typically comprises about one percent of the total plant flow volume, but 10-30% of the nitrogen load to the plant (Mulder et al. 2006). Because of the relatively high ammonia concentration in side stream liquors, it is usually cost effective to treat the side stream to remove ammonia (EPA, 2007). By treating the side stream liquor, the ammonia load to the plant is reduced and a source of nitrifying bacteria for bioaugmentation of the activated sludge process is produced. A separate report, “Side Stream Processes for Ammonia Removal: a Literature Review” (2009) presents detailed descriptions of several side stream nitrification processes that can serve as sources for bioaugmentation of the activated sludge process to achieve nitrification in the HPOAS process. Nitrification of Plant A SSB and BRF return side streams to reduce return ammonia load to the plant holds significant potential for cost effectively reducing ammonia discharge. The waste sludge from the side stream treatment process could be used for bioaugmentation to induce nitrification in the HPOAS process, reducing the ammonia load to the plant and nitrifying the remaining ammonia during secondary treatment.

Another approach to achieving nitrification in activated sludge processes under challenging conditions is the integrated fixed film activated sludge (IFAS) process. IFAS is being used to successfully achieve year-around nitrification in cold weather locations. Cold water temperatures can inhibit nitrification in activated sludge systems due to the slow growth rate of nitrifying bacteria. Nitrification using fixed film processes functions well in cold environments because the sludge age for fixed films is long. The IFAS process is a hybrid fixed film, suspended growth process that provides a location for development of submerged, fixed film colonies to grow in the activated sludge reactor. Fixed media is installed in the activated sludge aeration tank to facilitate the attached growth. In cold water conditions, nitrification is maintained by the nitrifying bacteria in the fixed film colonies (Randall and Sen, 1996). Incorporating the IFAS process into a HPOAS system holds the potential to achieve nitrification. Sears et al. (2003) reported that nitrifying bacteria can acclimate to the low pH environment of the HPOAS reactor, given enough time to establish viable populations in the reactor. Nitrifiers growing in fixed films would not be washed out of the system, giving them time to acclimate and begin nitrification.

Tertiary Ammonia Removal

An alternative to integrating nitrification into the activated sludge process is tertiary ammonia removal, adding a separate stage of treatment following secondary treatment (Muller, 2005). Tertiary ammonia removal process retrofits have been a successful solution for many plants faced with new ammonia discharge requirements. Retrofitted biological processes include nitrifying trickling filters, rotating biological contactors, biological aerated filters, and moving bed bioreactors. Physical-chemical processes for ammonia removal, successfully implemented, include ion exchange and breakpoint chlorination.

Nitrifying bacteria are autotrophic, aerobic organisms, meaning they need an oxygen source but they don't need an external organic carbon food source. Therefore, nitrification can be carried out using aerobic post secondary treatment. Biological aerated filters (BAF) have been successfully employed for tertiary nitrification in large wastewater treatment plants. A BAF is an aerated, upflow filter containing mineral or polystyrene media that supports growth of fixed film, nitrifying bacterial populations. Secondary effluent containing ammonia flows through the filter, contacting the biomass, which oxidizes the ammonia to nitrate. BAFs added to the 188 mgd Manchester,

UK, secondary wastewater treatment plant successfully reduce ammonia from 20 mg/L to less than 1 mg/L (Payraudeau et al., 2001). The Tahoe-Truckee wastewater treatment plant employed tertiary BAFs to reduce ammonia from a range of 10 – 34 mg/L to <0.5 mg/L. The reported aeration requirement for the Tahoe-Truckee BAFs was 30 g of oxygen for every gram of $NH4^+$-N oxidized for optimal nitrification (Holloway et al., 2008). Ganley et al. (2007) reported the successful start-up and operation, beginning in 2003, of an 84 mgd tertiary two-stage BAF, for nitrification and denitrification at the Syracuse, NY wastewater treatment facility. The BAF has performed well, not exceeding effluent ammonia discharge limits in three years of operation, and has been able to accommodate flow swings from 50 mgd to 150 mgd in a matter of hours without experiencing performance problems.

The BAF process has been reported to be capable of supporting autotrophic nitrification and denitrification by controlling dissolved oxygen levels in the filter. Aerobic nitrifying organisms live on the biofilm surface in a limited oxygen environment and anoxic denitrifying organisms live deeper in the biofilm. Nitrifying organisms partially nitrify some of the ammonium to nitrite, which the denitrifying organisms then use as an electron acceptor for oxidizing the remaining ammonium. This synergistic process enables the filter to perform total nitrogen removal, producing nitrogen gas, without the need for carbon supplementation (Han et al., 2001).

Nitrifying trickling filters (NTF) are another example of a biological tertiary treatment process that has been successfully employed for tertiary treatment ammonia removal. Nitrifying trickling filters are a well established treatment process. Evans et al. (2001) reported the 10-year performance of NTFs in meeting ammonia discharge permit limits at the Ames, Iowa wastewater treatment plant. The Ames NTF serves as tertiary treatment following trickling filter-solids contact secondary treatment. Ammonia reduction occurs in both secondary and tertiary treatment, with the NTF polishing the effluent by removing 14% of the total plant ammonia load. Parker et al. (1989) reported development of a design model for biofilm controlled nitrifying trickling filters with cross flow media and backwash that eliminates the need for subsequent clarification.

Moving bed biofilm reactor (MBBR) technology has been applied successfully for tertiary nitrification (Falletti and Conte, 2007; Andreottola et al., 2003). The MBBR process is characterized by an aerated reactor tank containing submerged plastic media with a high specific area for hosting biofilm populations. The media is retained in the reactor tank, which allows ample time for development of robust populations of slow growing, attached growth nitrifying bacteria. Kaldate et al. (2008) reported successful pilot testing of tertiary nitrification of HPOAS wastewater using MBBRs at the Harrisburg, PA wastewater treatment plant. Because the study was a pilot test, various media fill fractions for the reactor were used and ammonia and hydraulic loading rates were varied significantly, with the express objective of stressing the process to test its performance. The MBBR reliably removed ammonia from the HPOAS effluent under varying conditions, always maintaining the effluent ammonia concentration below 5 mg/L and generally below 1 mg/L. Bonomo (2000) investigated using high purity oxygen in MBBR nitrification of secondary effluent and determined that increased nitrification rates resulted, which could translate to smaller MBBR reactors.

Rotating biological contactors (RBC) is another attached growth biological treatment process that has been employed for tertiary nitrification. Boller et al. (1990) reported that the nitrification rates of trickling filters could be doubled by RBCs. In a full scale implementation in Switzerland using RBCs for tertiary nitrification, performance was good and no need for subsequent clarification was needed.

Physical-Chemical Treatment

Ion Exchange is a process in which ions on the surface of a fixed solid resin matrix are exchanged for ions of similar charge from a process fluid passed through an ion exchange vessel containing the resin matrix. When ammonium ions in secondary effluent come in contact with the resin matrix, the cation attached to the matrix is released to solution in exchange for the ammonium ion, which is sequestered in the resin matrix (Jorgensen and Weatherly, 2003). When the ion exchange resin becomes saturated with exchanged ammonium ions, the vessel is regenerated and returned to service (Ramisetty, 1999). The regeneration process produces an ammonia-rich solution that can be combined with sulfuric acid to produce ammonium sulfate, which can be sold as fertilizer or discharged with treated municipal sludge (Carrio et al. 2003). Natural and synthetic ion exchange solids can be used for the removal of ammonium ions from solution. Jorgensen and Weatherly (2003) demonstrated that synthetic resins most effectively removed ammonium from wastewater and that uptake was enhanced in the presence of organic ammonia.

Break-Point Chlorination is a process in which chlorine is used to oxidize ammonia to nitrogen gas. In separate studies, Brooks (1999) and Pressley et al.(1972) reported that the effective chlorine dose ratio for breakpoint chlorination was 8:1 mg/L Cl_2 : mg/L NH_3-N. Treated effluent can contain many constituents that exert a chlorine demand, which will increase the dose required to achieve both disinfection and complete ammonia oxidation. In Brooks' study at the Centreville, Virginia wastewater treatment plant, the breakpoint reaction required 30-35 minutes to achieve ammonia concentrations of <0.2 mg/L NH_3-N at 8°-12°C. Advantages of the process are its ability to obtain near-zero ammonia concentrations in the treated effluent, and that most wastewater treatment plants have chlorination systems already in place. Disadvantages include chemical costs for chlorination and dechlorination, comsumption of alkalinity, increase in dissolved solids, and inability to remove nitrite and nitrate.

Conclusions

Ammonia removal in a high purity oxygen activated sludge system is more difficult than in an air activated sludge system. Low mixed liquor pH, resulting from CO_2 accumulation in covered tanks, and short MCRT operation inherent in HPOAS processes inhibit nitrification. HPOAS facilities, faced with a requirement to reduce ammonia, have found a variety of methods to accomplish it. Bioaugmentation of the HPOAS biomass with nitrifying bacteria from an outside source is one successful approach. Proven nitrifying organism sources have been waste sludge from side stream nitrification treatment of solids dewatering and processing streams and from dissolved air activated sludge processes. Integrated fixed film activated sludge treatment is another augmentation approach that provides an environment for nitrifying organisms to grow. In the IFAS process, nitrifying biofilms grow on fixed media within the HPOAS reactor.

Another approach to achieving ammonia removal in an HPOAS facility is tertiary treatment. Tertiary biological nitrification has been successfully employed by HPOAS plants needing to nitrify. Biological aerated filters provide a media source with ample surface area for nitrifying organisms to become established and to effect nitrification of secondary effluent. Nitrifying trickling filters and rotating biological contactors operate under a similar principle, effecting nitrification of secondary effluent by passing it over nitrifier-rich biofilm-covered media. Finally, moving bed biofilm reactors have also proven successful as a tertiary process for removing ammonia. MBBRs are characterized by biofilm-coated, high specific area media, submerged in an aerated reactor.

Two tertiary solutions fall under the classification of physical-chemical processes. The first is ion exchange. Secondary effluent is passed through an ion exchange vessel in which ammonium ions are retained, in exchange for a positively charged ion that is released into the effluent. Breakpoint chlorination is another physical-chemical ammonia removal process that has been successfully employed as tertiary treatment. Breakpoint chlorination is used to oxidize ammonia, converting it to nitrogen gas.

Each of the identified processes has worked for different facilities. Many variables come into play in selecting the best process for any particular facility, including cost, available area, and compatibility with existing processes. By identifying a rich source of possible solutions for meeting a requirement to reduce ammonia discharges from Plant A, plant staff and design consultants will be assisted in selecting the best solution for Plant A, benefitting from the experiences of other facilities that were faced with similar requirements.

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