

Methanol Use in Denitrification

Effective Use to Clean Our Waterways

Importance of Denitrification

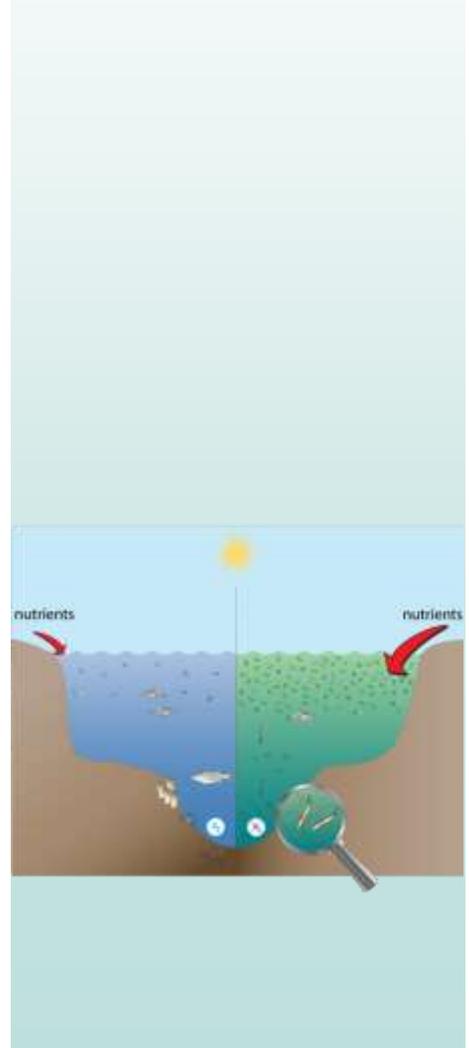
In 2012, the Gulf of Mexico “Dead Zone,” an area of eutrophication (excessive plant/algae growth) and hypoxia (oxygen depletion), spans some 6,700 square miles (17,300 square kilometers) from the mouth of the Mississippi River. Marine dead zones can be found in more than 400 estuaries worldwide including the Chesapeake Bay, Long Island Sound, Baltic Sea, Black Sea, Caspian Sea, Mediterranean Sea, East China Sea, and the South China Sea. These dead zones are caused by nutrient enrichment, particularly nitrogen and phosphorous, that comes from agricultural run-off and major point sources such as wastewater treatment plants.

Facing regulatory pressure, municipal wastewater treatment plant operators around the globe are increasingly turning to a process of biological nutrient removal or “denitrification” that is based on the addition of methanol as a carbon source to accelerate the biodegradation of nitrogen. The Methanol Institute engaged the environmental consulting firm Exponent to prepare a 124-page white paper titled “Methanol in Wastewater Denitrification,” providing a comprehensive overview of the use of methanol in the removal of nitrogen from wastewater.

Denitrification around the World

The last several decades have seen a worldwide increase in the regulatory control of nitrogen from municipal wastewater treatment plants. In the United States, the Clean Water Act implements water regulation by incorporating both technology-based and water-quality-based levels of treatment. Historically, most WWTPs have treated to standards based on the ability of secondary treatment to meet effluent standards, such as 30 mg/L for both biological oxygen demands (BOD) and total suspended solids.

As the impact of the macronutrients nitrogen and phosphorus on eutrophication – a term used to describe when aquifers and waterways gain too much nutrient from sewage and wastewater - has become more apparent, the U.S. Environmental Protection Agency began to put more emphasis on meeting water-quality-based standards. With too much



nutrient in waterways, surface plant life can grow rapidly starving the water of oxygen and sunlight.

Given the regional nature of sources for impacted estuaries, the most effective way to control the amount of nitrogen effluents is through collaborative efforts of multiple jurisdictions. The Chesapeake Bay and Long Island Sound programs are examples of coordination by state and local agencies to reduce the total load of reactive nitrogen to regional water bodies, which includes the upgrading of WWTPs to remove nitrogen from their effluents.

The Blue Plains Wastewater Treatment Facility, one of the largest in the United States, continually meets, if not exceeds national standards for nitrogen loadings in water each year. Furthermore, the addition of methanol to the denitrification process has saved Blue Plains, and many plants like it, millions of dollars over the long-term.

In Europe, the European Water Framework Directive (EU WFD) marked a shift in focus, from point-source control to an integrated prevention and control approach at the water-body level. As a result, tertiary wastewater treatment has increased since 1990, although the percentage of wastewater treatment plants with tertiary treatment varies by region. The EU WFD caused the discharge standard for nitrogen in water to decrease from 10 mg/L to 2.2 mg/L. The goal of this action is to “promote sustainable water use, protect the aquatic environment, improve the status of aquatic ecosystems, mitigate the effects of floods and droughts, and reduce pollution.” The two- step strategy to achieve the directive’s goals includes the adoption of new wastewater treatment technologies which includes biological denitrification.

In China, expanding industrialization has resulted in a rising need for discharge standards and more effective wastewater treatment. As of 2002, 35.5% of rivers in China were not suitable for drinking-water use due to pollution issues, which has led to water shortages. Environmental legislation put in place in 2003 sets Class 1A effluent discharge standards at <5 mg/L ammonia nitrogen and <15 mg/L total nitrogen. As of 2002, only 39% of wastewater in China was being treated; the number grew officially to 59% as of 2008. In the last several years, almost a dozen existing WWTPs have been upgraded to biologically remove nitrogen using denitrification filters, with methanol as the supplemental carbon source.



Denitrification Process

In order to meet mandated ammonia discharge requirements, most municipal systems in the United States practice nitrification, which adds additional nitrogen to the water. However, only about five percent of Nr is removed through engineered treatment systems. A tertiary nitrogen removal system presents a method for removing a large portion of the nitrogen concentration from wastewater effluent before it is discharged. Through a process known as "denitrification," water treatment facilities convert the excess nitrate into nitrogen gas which is then vented into the atmosphere.

The removal of nitrogen in biological treatment systems consists of four basic steps. The first step is the conversion of organic nitrogen to ammonia in a process called ammonification. Ammonia is then converted to nitrate in a two-step aerobic process called nitrification—the conversion of ammonia to nitrite followed by the conversion of nitrite to nitrate. Finally, conversion and removal of nitrate can be carried out using various treatment configurations. All treatment systems, however, require an aerobic zone for converting ammonia to nitrate and an anoxic zone for converting the nitrate to nitrogen gas. One of the more common approaches to retrofitting existing facilities is to extend the aeration period to allow for nitrification, followed by a filtration system for denitrification. Because organic carbon is consumed mostly in the extended aeration process, it is often necessary to add a carbon source, such as methanol, especially when the discharge requirements for total nitrogen are low.

Role of Methanol

As part of the denitrification process, methanol plays a crucial role in reducing environmentally-damaging effluent that is discharged by wastewater treatment facilities across the globe. Methanol is a naturally occurring, biodegradable molecule and is employed in these operations because of its favorable chemical properties. Nearly 200 wastewater treatment facilities across the United States are currently using methanol in their denitrification process. Methanol is the most common organic compound used in denitrification, accelerating the activity of anaerobic bacteria that break down harmful nitrate. In an anoxic tertiary nitrogen removal system, an external carbon source, such as methanol, is often required to ensure that denitrification is maximized.



Life Cycle Assessment (LCA) Results

The three common external carbon sources, capable of removing nitrogen from wastewater, methanol, ethanol and acetic acid were examined for tertiary nitrogen removal by using a life-cycle assessment (LCA). LCA is a tool that allows for the impacts of a product or process to be compared across different life stages and impact categories. This ensures that the environmental burden is not being shifted from state to state, or location to location, in pursuit of environmental goals, and allows for the overall impact of the product to be examined.

LCA was used to evaluate the following nine impact categories: ozone depletion, global warming, acidification, eutrophication, smog formation, ecotoxicity, particulate respiratory effects, human carcinogenic effects, and human non-carcinogenic effects. In terms of environmental impact, they are not all the same. In the nine impact categories presented, methanol has the lowest impact in eight of the categories. The exception to this is ozone depletion, where ethanol has the lowest impact. Acetic acid has the greatest impacts in seven of the categories, with the exception of acidification and eutrophication, where ethanol has the highest impact. In terms of relative environmental impact among the three external carbon sources, methanol has the lower impact in most categories, with acetic acid having the greatest impacts.

