

**Abstract**

Since the mid-1990s, constructed wetlands have been increasingly used as a low energy 'green' technique, in the treatment of wastewater and storm water, driven by the rising cost of fossil fuels and increasing concern about climate change. Among various applications of these wetlands, a significant area is the removal of nitrogenous pollutants to protect the water environment and to enable effective reclamation and reuse of the wastewater. It is economical water treatment method. This paper provides a review of the current state of nitrogen removal technology, focusing on existing types of wetlands, the mechanisms of nitrogen removal, major environmental factors relative to nitrogen removal, and the operation and management of the wetlands. Keywords: Nitrogen removal / Subsurface flow / Wastewater treatment

**Keywords:** Aquatic plant, Macrophyte, Nutrient removal, Phytoremediation, Wetland

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**1 INTRODUCTION**

Most wastewaters, such as industrial and agricultural wastewater, urban drainage, sewage, and landfill contain nitrogenous compounds that have given rise to various negative phenomena in water environments, it disturbed the aquatic life e.g. damage to aquatic life, being toxic to fish and/or causing oxygen depletion in receiving water biota. In wastewater treatment wetlands, the efficiency of organic matter removal often meets the specified design target, but the efficiency of nitrogen removal is mostly poor. In European systems, for example, typical removal percentages of ammonia cal-nitrogen in long-term operation is only 35%, or up to 50% after modifications are made specifically to improve nitrogen removal. Similarly, storm water wetlands typically remove only around 45% of total nitrogen, most of which is made up of particulate organic nitrogen. In order to understand and improve the performance of the wetlands, it is necessary to briefly look back at the history of this technology and look into the mechanisms of pollutant removals. for increasing efficiency of the nitrogen removal In doing this, we aim to identify critical knowledge gaps, as well as potential areas worthy of future exploration and development

**1.2 Increasing applications driven by cost of fossil fuels and climate change**

Since the 1990s, the applications of constructed wetlands have expanded radically, due to the rising cost of fossil fuels and increasing concern about climate change, which provide a financial incentive, as well as public support, to the implementation of this low energy consumption 'green' technique. Constructed wetlands have now been successfully used in the treatment of several wastewaters such as domestic sewage, urban runoff and storm water, industrial and agricultural wastewater

**1.3 Constructed wetland: a bioreactor**

A constructed wetland is considered to be a bioreactor. A various number of physical, chemical, and biological processes with microbial communities, emergent plants, soil, and

sediments accumulated in the lower layer take place in the systems. Nitrogen concentration is often of concern because of its potential to cause adverse effects in receiving water systems. it disturb aquatic life Among various nitrogen groups, dissolved inorganic nitrogen species like nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ), and ammonia ( $\text{NH}_3$ ) or ammonium ( $\text{NH}_4^+$ ) – rather than particulate organic nitrogen – have the greatest impact on aquatic systems, because they are easily available for uptake by microorganisms. Many researchers have shown the impact of excessive nitrogen loads on receiving waters. The removal of organic substances, typically 80–90%, is now satisfactory in constructed wetlands because of gradual improvement over two decades. However, the nitrogen removal rates are often unsatisfactory. A variety of nitrogen forms in constructed wetlands can be removed through specific treatment processes, such as combined nitrification-denitrification and sedimentation, particularly at the sediment-water and water-plant interface. there are many nitrogenous compound are present in water body.

**1.5 Constructed wetland performance and processes**

It necessary to understand the performance of the nitrogen removal processes The big unknowns Since nitrogen-rich discharges into receiving water systems are responsible for a variety of environmental problems, optimizing nitrogen removal is a critical objective. So far, activated sludge and bio film processes have been the main focus for biological nitrogen removal. However, these processes are expensive, particularly when employed in medium and small communities. Constructed wetlands have proven potential for nitrogen removal, but nitrogen removal efficiency has been inconsistent, due to inadequate observation of nitrogen transformation and removal mechanisms. There are still many unknown parts related to constructed wetlands performance, diverse driving operations, and nitrogen constraints. Therefore, it is necessary to explore explicit nitrogen transformation mechanisms based on consideration of kinetics

and the interactions between microbial communities and emergent plants.

## 2. PROCESSES OF NITROGEN REMOVAL

The two biological processes are involved in the processes of nitrogen removal. Nitrogen removal is achieved by two major processes, physicochemical and biological treatment techniques. Traditional biological nitrogen removal from water and wastewater, primarily composed of a combination of aerobic nitrification and anaerobic denitrification, is usually considered to accomplish optimal and economic nitrogen treatment. However, there are still many unresolved issues, such as the requirement of an extra carbon source in wastewater with low C/N ratio, the requirement for large treatment areas, and high maintenance cost. Most wastewaters do not have enough biodegradable carbon and an external organic source to carry out heterotrophic denitrification. In nitrogen removal treatment, biological processes frequently have several obstacles because of lower energy consumption and high cost in the wastewater treatment plant. Consequently, many studies on the mechanisms of the nitrogen cycle – not only nitrification and denitrification but also new sustainable processes – are being conducted. The removal process of pollutants in the SSF wetland system is complex and dynamic, with many variables. The forms of nitrogen in natural ecosystems are illustrated; this is a green technique. Total nitrogen in the natural state can fall into two basic groups, total Kjeldahl nitrogen and oxidized nitrogen (NO<sub>x</sub>). Organic nitrogen is subdivided into particulate organic nitrogen (PON) and dissolved organic nitrogen. Nitrate and nitrite are soluble inorganic nitrogen and, coupled with ammonia and ammonium, form the dissolved inorganic nitrogen (DIN). Total dissolved nitrogen builds up; DON, NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup>, and NO<sub>x</sub> are known to be highly bio-available. Many studies reported that water purification mechanisms in constructed wetlands are achieved by hydrophytes and microorganisms around the plant root zone, along with physical precipitation. The major nitrogen treatment mechanisms of constructed wetlands include microbial interactions with nitrogen, sedimentation, chemical adsorption, and plant uptake. The central pathways for nitrogen removal in constructed wetlands are nitrification followed by denitrification. In constructed wetlands, nitrogen removal ranges from 25 to 85%. In constructed wastewater wetlands, the denitrification process may remove 60-70% of the total removal nitrogen and 20-30% of that is derived from plant uptake. In storm water wetlands, the proportion of nitrogen removed by wetlands is considered to be considerably lower. The mass budget for nutrients indicates that 14% is originated by physical treatment process and 8.6% by plant uptake; i.e., the absorbed amount of nitrogen into the plant itself.

### 2.1 Biodegradation: classic routes

The nitrogen removal mechanisms in constructed wetlands is known to involve ammonification, nitrification-denitrification, plant uptake, and physicochemical methods such as sedimentation, ammonia stripping, breakpoint chlorination, and ion exchange. A nitrogen conversion diagram for constructed wetlands.

#### 2.1.1 Ammonification

Ammonification is the process where organic N is biologically converted into ammonia. Pollutants containing nitrogen are

readily degraded in both aerobic and anaerobic zones of reed beds, releasing inorganic ammonia-cal-nitrogen (NH<sub>4</sub>-N). The inorganic NH<sub>4</sub>-N is mainly removed by nitrification-denitrification processes in constructed wetlands. Kinetically, ammonification proceeds more rapidly than nitrification. The rates of ammonification is fastest in the oxygenated zone and then decrease as the mineralization circuit changes from aerobic to facultative anaerobic and obligate anaerobes. The rates are influenced by temperature, pH, C/N ratio, available nutrients, and soil structure. NH<sub>4</sub>-N in SSF systems can be reduced by other processes, which include adsorption, plant uptake and volatilization. However, it is generally believed that the contribution of these processes to the NH<sub>4</sub>-N removal is very limited compared with nitrification-denitrification.

#### 2.1.2 Nitrification

Nitrification is the biological oxidation of ammonia or ammonium to Nitrite followed by the oxidation of the nitrite to nitrate. The transformation of ammonia to nitrite is usually the rate limiting step of nitrification. Nitrification is an important step in the Nitrogen cycle in soil. Nitrification is an aerobic process performed by small groups of autotrophic bacteria and archaea. Decomposition processes in the wetlands are believed to convert a significant part of the organic nitrogen to ammonia. Biological nitrification, which is performed by nitrifiers such as Nitrosomonas, Nitrospira, Nitrosococcus and Nitrobacteria, followed by denitrification is believed to be the major pathway for ammonia removal in both SF and SSF constructed wetlands. In traditional nitrogen treatments, the biological nitrogen removal requires a two-step process: nitrification followed by denitrification. Nitrification implies a chemolithoautotrophic oxidation of ammonia to nitrate under strict aerobic conditions and is performed in two sequential oxidative stages: ammonia to nitrite (ammonia oxidation) and nitrite to nitrate (nitrite oxidation). Each stage is performed by different bacterial genera which use ammonia or nitrite as an energy source and molecular oxygen as an electron acceptor, while carbon dioxide is used as a carbon source. The most commonly recognized genus of bacteria is that of Nitrosomonas for the ammonia oxidation process and Nitrobacter for the nitrite oxidation process. NO<sub>3</sub> The nitrification process is very oxygen demanding. Oxygen consumed in this process is 3.16 mg O<sub>2</sub>/mg NH<sub>4</sub>-N oxidized and 1.11 mg O<sub>2</sub>/mg NO<sub>2</sub>-N oxidized. Moreover, yields produced by Nitrosomonas and Nitrobacter are 0.15 mg cells/mg NH<sub>4</sub>-N oxidized and 0.02 mg cells/mg NO<sub>2</sub>-N oxidized, respectively. In addition, alkalinity is needed as 7.07 mg CaCO<sub>3</sub>/mg NH<sub>4</sub>-N oxidized. However, the alkalinity reduction by the acid made in the nitrification process can cause a deep pH reduction. The pH value is very important in the nitrification reaction since nitrification rates swiftly decline where the pH drops to lower than 7.0. Thus, the appropriate chemicals such as lime should be replenished when the alkalinity in the process is reduced by the acid produced in the nitrification reaction. The doubling time of nitrifying bacteria is reported as 2–6 days. The nitrifying bacteria of the autotroph group have much lower respiration rates than the heterotrophs, which are responsible for BOD removal. Accordingly, in the SSF systems, significant nitrification generally does not take place before substantial BOD reduction. The rate of nitrification is influenced by

temperature, pH, alkalinity, inorganic carbon source, moisture, microbial population, and concentrations of ammonium-N and dissolved oxygen. The ammonia uptake rate (AUR) varies with reactor configuration, substrate type, and influent ammonium concentration.

### 2.1.3 Denitrification

The biological denitrification mechanism makes use of nitrate as the terminal electron acceptor in low-oxygen environments. Denitrifying bacteria decrease inorganic nitrogen such as nitrate and nitrite into innocuous fundamental nitrogen gas. Denitrifying bacteria (denitrifiers) can be classified into major species, heterotrophy and autotrophs. Heterotrophs are microbes that need organic substrates to obtain their carbon source for growth and evolution, and get energy from organic matter. In contrast, autotrophs utilize inorganic substances as an energy source and CO<sub>2</sub> as a carbon source. So far, the heterotrophic denitrification process has been mainly engaged in conventional wastewater treatment plants, while autotrophic denitrification has only recently been studied. The second step, denitrification, is conducted by a heterotrophic microorganism, conditions. The proportion of total nitrogen removal by denitrification is typically 60–95%, in comparison to 1–34% assimilated by plants and algae. Heterotrophic microorganisms utilize an oxidized form of nitrogen, NO<sub>2</sub>, NO<sub>3</sub>, as terminal electron acceptor and organic carbon as electron donor under anoxic conditions. Consequently, the denitrification provides energy to denitrifiers and it is also affected by the organic matter of the electron donor. This process is shown in the following. Denitrification can only take place in the anoxic zones of the systems, as the presence of dissolved oxygen suppresses the enzyme system required for this process. High concentrations of nitrate in the inlet zones can lead to more vigorous and robust populations of denitrifiers within the inlet sediments. In constructed wetlands, it is believed that microsites with steep oxygen gradients can be established, which allow nitrification and denitrification to occur in sequence, in very close proximity to each other. Sufficient organic carbon is needed as an electron donor for nitrate reduction, which provides an energy source for denitrification microorganisms. This carbon source can be available in reed beds from organic pollutants of wastewater or cell materials of microorganisms. The rate of denitrification is influenced by many factors, including nitrate concentration, microbial flora, type and quality of organic carbon source, hydroperiods, different plant species residues, the absence of O<sub>2</sub>, redox potential, soil moisture, temperature, pH value, presence of denitrifiers, soil type, water level, and the presence of overlying water. Numerous studies have shown that the denitrification rate in organic carbon-restricted water and wastewater can be improved continually by supplementing any carbon sources, even though there are some issues regarding external organic carbon sources in heterotrophic denitrification. Currently, there is much attention towards biological nitrogen removal, whilst the denitrification process is generally time-consuming, especially for industrial wastewaters involving much nitrate. Also, a number of researchers have studied denitrification systems, including the application of granular activated carbon, packed beds, and rotating biological contractors. These attempts are developing

and some new systems such as membrane bio film reactors have been established].

### 2.1.4 Biodegradation:

The term is often used in relation to: biomedicine, Water management, ecology, and the Bioremediation of the natural environment. It is now commonly associated with environmentally-friendly products, capable of decomposing back into natural elements. Anammox Routes The Anammox (anaerobic ammonium oxidation) process provides a potential alternate process for improving total nitrogen removal. The recent discovery of Anammox bacteria opened up a new avenue in the study of nitrogen transformations. Denitrification by Anammox bacteria is now proven to be partly responsible for the transformation of ammonia into nitrogen gas within the nitrogen cycle. In this process, ammonium is autotrophically oxidized to nitrogen gas while nitrite is employed as an electron acceptor under anaerobic conditions. Thus, there is no demand for aeration and addition of an external carbon source, resulting in a cost saving and preventing insufficient conversion of organic substances. The Anammox bacteria, such as *Candidatus* *Brocadia* *anammoxidans*, *Planctomycetes* spp., *Thiobacillus* *denitrificans*, *Thiomicrospira* *denitrificans*, *Thiosphaera* *aponotropha*, and *Paracoccus* *denitrificans*, are autotrophic, in contrast to classic denitrifiers which are mostly heterotrophic and thus need organic carbon for their carbon and energy supply. Therefore, stimulating Anammox bacteria in a wastewater treatment system reduces the need for an organic carbon source, which is required in the conventional denitrification process. In these processes with partial nitrification in one reactor, such as Anammox (anaerobic ammonium oxidation), Sharon (single-reactor high-activity ammonia removal over nitrite), and Oland (oxygen-limited autotrophic nitrification-denitrification), single-stage autotrophic nitrogen removal is accomplished through assistance between aerobic ammonia oxidizing bacteria and Anammox bacteria. However, a strict controlled environment and reactor arrangement are needed, as Anammox bacteria have a slow growth rate. In reality, the Anammox process has been reported to produce higher removal efficiency of total nitrogen, and to save up to 90% of operation cost, due to a reduction of the input of organic matter. When the Anammox bacteria co-function with autotrophic nitrosobacteria via the following route in a single reactor, the removal pathway is known as 'completely autotrophic nitrogen removal over nitrite'. The key operating factors of partial nitrification processes (i.e. Anammox and CANON) include temperature, pH, free ammonia, free nitrous acid, hydraulic residence time (HRT), dissolved oxygen, salt, organic compounds, and hydroxylamine. Further research on the selection of Anammox bacteria species and optimal operating parameters is needed to stimulate novel nitrogen removal routes in constructed wetlands.

### 3. PLANT UPTAKE

In plants, mineral uptake is the way in which minerals enter the cellular material, typically following the same pathway as water. The most normal entrance portal for mineral uptake is through plant roots. (Roots, 2005) Some mineral ions diffuse in-between the cells. The uptake of ammonia and nitrate by macrophytes converts inorganic nitrogen forms into organic

compounds, as building blocks for cells and tissues ]. The capability of rooted plants to use sediment nutrients partly explains their extensive yield compared with planktonic algae in many systems . Various plant species differ in their favoured forms of nitrogen absorbed, depending on the forms available in the wetland. The  $\text{NH}_4^+$  preference is common in macrophytes living in environments with limited nitrification, where  $\text{NH}_4^+$  is abundant . The uptake and storage rate of nutrients by plants depend on the nutrient concentration of their tissues. Thus, desirable features of a plant used for nutrient assimilation and storage Eng. Life Sci. 2009, 9, No. 1, 11–22 Constructed wetland 15 & 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim <http://www.els-journal.com> include fast growth, high tissue nutrient content, and the ability to obtain a high-standing crop. Conversely, plants that have great biomass accumulation during autumn and winter may release much of their accumulated nitrogen back into the water during the winter season .

#### 4.CONCLUSION

The newly discovered Anammox and CANON processes offer significant potential for improved nitrogen removal efficiency and treatment performance in various aquatic systems; however, more research is needed to investigate and explore this process in constructed wetlands. Specifically, studies are needed to identify the growth conditions of Anammox bacteria and to determine design parameters for promoting the conditions. Further research is also required on the predominant microbial species and hydrophytes having a specific gene for nitrogen removal, using biogenetical techniques through gene modification of microbial-planted systems in order to improve process performance and the efficiency of the nitrogen removal in constructed wetlands. Advances in this area may help to optimize nitrogen removal and may reduce the drawbacks and imbalances with the natural ecosystem. To optimize nitrogen removal, the kinetics

study, based on mass balance analysis for components of nitrogen transformation processes occurring within the constructed wetland treatment cells using the isotope-tracking  $^{15}\text{N}$  technique, will provide mechanistic information for nitrogen transformations. This pattern of details will be necessary to develop the design and better management of aquatic environments. Further investigations are needed to evaluate the sustainable removal performance by long-term monitoring for water quality, development of scale-up techniques, and an actual proof test based on the experimental results at pilot scale. Studies on these fields will contribute greater insights into the nutrients treatment process in constructed wetlands.

#### REFERENCES

- [1] G. D. Taylor, T. D. Fletcher, T. H. F. Wong, P. F. Breen, Nitrogen composition in urban runoff – implications for stormwater management, *Water Res.* 2005, 39, 1982–1989.
- [2] J. T. A. Verhoeven, A. F. M. Meuleman, Wetlands for wastewater treatment: Opportunities and limitations, *Ecol. Eng.* 1999, 12, 5–12.
- [3] V. Luederitz, E. Eckert, M. Lange-Weber, A. Lange, R. M. Gersberg, Nutrient removal efficiency and resource economics of vertical flow and horizontal flow constructed wetlands, *Ecol. Eng.* 2001, 18, 157–171.
- [4] P. M. Nuttall, A. G. Boon, M. R. Rowell, Review of the Design and Management of Constructed Wetlands. CIRIA Publications, London, UK 1998, 62–67.
- [5] P. F. Cooper, B. C. Findlater, Constructed Wetlands in Water Pollution Control. Pergamon Press, Oxford, 1990.
- [6] M. Scholz, B. H. Lee, Constructed wetlands: A review, *Int. J. Environ. Stud.* 2005, 62, 421–447.
- [7] J. P. Heaney, L. Wright, D. Sample, Research needs in urban wet weather flows, *Water Environ. Res.* 1999, 71, 241–250.