Nitrogen

Review

Technologies for Biological and Bioelectrochemical Removal of Inorganic Nitrogen from Wastewater: A Review

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Abstract: Water contamination due to various nitrogenous pollutants generated from wastewater treatment plants is a crucial and ubiquitous environmental problem now-a-days. Nitrogen contaminated water has manifold detrimental effects on human health as well as aquatic life. Consequently, various biological treatment processes are employed to transform the undesirable forms of nitrogen in wastewater to safer ones for subsequent discharge. In this review, an overview of various conventional biological treatment processes (viz. nitrification, denitrification, and anammox) have been presented along with recent novel bioelectrochemical methods (viz. microbial fuel cells and microbial electrolysis cells). Additionally, nitrogen is an indispensable nutrient necessary to produce artificial fertilizers by fixing dinitrogen gas from the atmosphere. Thus, this study also explored the potential capability of various nitrogen recovery processes from wastewater (like microalgae, cyanobacteria, struvite precipitation, stripping, and zeolites) that are used in industries. Further, the trade-offs, challenges posed by these processes have been dwelt on along with other biological processes like CANON, SHARON, OLAND, and others.

Keywords: nitrification; denitrification; annamox; microbial fuel cells; CANON; SHARON; OLAND; nutrient recovery

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1. Introduction

The drastic increase in world population has led to intense industrialization and subsequent generation of wastewater from various sources. The generated wastewater is highly nutrient-rich in terms of ammonia, nitrate, nitrite, and other pollutants which need treatment before being discharged. Unless adequately treated, the nitrogenous pollutants from the wastewater can lead to eutrophication, cause methemoglobinemia or blue-baby syndrome, lead to oxygen depletion, aquatic toxicity, and have many other detrimental impacts on the environment [1–4]. Also, the aquaculture industry with intensive aquaculture practices further adds to the generation of wastewater saturated with nitrogenous contaminants [5,6]. The removal of these nitrogenous entities from wastewater can be conducted by various biological and physicochemical methods. However, the biological processes are more efficient and relatively cost-effective and hence globally adopted and preferred [7,8]. The biological methods of pollutant removal are generally employed for wastewater with low nitrogen concentration, with nitrification and denitrification being the most conventionally used ones. However, other processes of partial or combined nitrification/denitrification can also be used for nitrogenous removal [9–12]. Such avenues have been discussed in detail in this study.

In addition to this, energy is the most critical challenge that humanity of this century is facing. The challenges in the domain of energy scarcity have been explored by many studies worldwide [13–21]. These two challenges of nitrogenous contaminant removal and energy paucity can be simultaneously addressed by bioelectrochemical methods of wastewater

treatment [22,23]. These novel methods also consider that "misplaced resources" is the befitting epithet that can be attributed to waste. This is since they harness bioelectricity from wastewater while providing green solutions to urban problems like the removal and recovery of nitrogenous contaminants from water.

This review focuses on the various conventional processes of biological methods of removal along with their working mechanism, microorganisms involved, and process technologies utilized. Additionally, novel bioelectrochemical methods of removal have also been discussed along with processes of nitrogen recovery from wastewater. This study can aid wastewater engineers and water professionals in decision-making and adopting strategies depending on the prevailing scenario.

2. Conventional Biological Treatment Processes

2.1. Nitrification

Nitrification includes two successive biological oxidation steps: (1) oxidation of NH_4^+ to NO_2^- and (2) conversion of NO_2^- to NO_3^-. The first step is carried out by ammonium oxidizing bacteria (AOB, e.g., *Nitrosomonas*) with catalyzation by ammonia monooxygenase (AMO) [24–27] and hydroxylamine oxidoreductase (HAO) [28,29], along with the formation of the intermediate product hydroxylamine (NH_2OH). The second step of nitrification, which entails the formation of NO_3^-, is carried out by nitrite-oxidizing bacteria (NOB, e.g., *Nitrobacter*) in the presence of molecular oxygen. Catalyzation of this step is performed by nitrite oxidoreductases (NXR) and nitrite-oxidizing systems. NXR is an oxidation enzyme that occurs in *Nitrobacter* [30]. The reaction pathway of this process can be represented by: *Nitrosomonas*:

$$\textit{Nitrosomonas}: NH_4^+ + 1.5O_2 \rightarrow NO_2^- + H_2O + H_2^+ \quad (1)$$

$$\textit{Nitrobacter}: NO_2^+ \, 0.5O_2 \rightarrow NO_3^- \quad (2)$$

$$\text{Overall}: NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \quad (3)$$

The carbon requirements of nearly all nitrifiers are met by CO_2 fixation of the Calvin cycle, and their only source of energy is generated during the oxidation of ammonia [31]. As reported by researchers, 80% of this produced energy is consumed for CO_2 fixation, and for each fixed carbon atom, nitrifiers need to oxidize approximately 35 molecules of NH_3 or 100 molecules of NO_2^- [32,33]. Due to this sluggish growth rate of nitrifiers, their microbial colonization can take 4–8 weeks depending on external parameters such as water temperature, alkalinity, salinity, and other stresses [34,35].

Parallel as well as in contrast to the other wastewater treatment technologies used, nitrification comes with its own set of advantages and disadvantages. Cost-effectiveness of the process has trade-off in the form of the slow rate of reaction, the requirement of controlling oxygen concentration and the impact of other parameters on nitrification activity, and long hydraulic retention time (HRT) and long solids retention time (SRT). To diminish the energy input of this process, many studies [30,36,37] are being conducted in the domain of partial nitrification, which has an upper hand over conventional nitrification processes in the form of: (i) 40% reduction in chemical oxygen demand (COD); (ii) twice the rate of nitrite reduction in the following denitrification process; (iii) 300% reduction in biomass; and (iv) 20% CO_2 emission in the subsequent denitrification process. These studies also report that the partial nitrification process favors the growth and activity of AOB at the cost of inhibiting NOB (with the help of inhibitors like sulfide, hydroxylamine, salt, chlorate, hydrazine, etc. [38]. This is accomplished with consequent positive impacts of parameters like: (i) concentration of dissolved oxygen of about 1.5 mg/L (DO) [39]; (ii) temperature higher than 25 °C [40]; (iii) optimum pH range of 7.5 to 8.5 [36]; and (iv) optimum sludge retention time of 5 days (SRT) [41].

2.1.1. Participation of Microorganisms in Nitrification

The two-step process of aerobic nitrification is carried out by two phylogenetically unrelated groups, AOB and NOB. These chemolithoautotrophic microorganisms work in

tandem to convert ammonia to nitrite in the nitrification system Equations (1)–(3). Their syntrophic association aids each other in the context of energy: AOB produces the substrate (nitrite) that NOB can efficiently use and thus makes do with the poor energy generated during nitrite oxidation to nitrate. On the contrary, NOB can protect AOB from the toxicity of generated nitrite by inhibiting its buildup [42].

AOBs are characterized by multi-layered cell walls with flagella as their locomotory organ. Majorly, five genera of AOBs in two different subclasses of β and γ-Proteobacteria have been reported by researchers [43,44]. The β-subclass of AOB includes *Nitrosomonas* (e.g., *Nitrosococcus mobilis*), *Nitrosospira*, *Nitrisovibrio*, and *Nitrosolobus* [45]. On the other hand, literature reports the detection of *Nitrosococcus* clusters belonging to the γ-subclass [46,47]. Though more than 25 AOB species have been reported, nonetheless, *Nitrosomonas* and *Nitrobacter* remain the most widely studied [48,49]. The key enzymes of AOB involved in the conversion of ammonia to nitrite are AMO and HAO. AMO is a membrane-bound hetero-trimeric copper enzyme, whereas HAO is positioned in the periplasm [36].

NOBs are more diverse and prevalent than AOBs in Proteobacteria [47]. Literature reports eight species of NOB and four phylogenetically varied groups [50]. The genera *Nitrococcus* and *Nitrobacter* have been allotted to the α- and γ-subclasses of Proteobacteria, respectively. Until recently, *Nitrobacter* was considered to be the most important one. However, recent studies have reported *Nitrospira* to be the most prevalent NOB in wastewater treatment plants (WWTPs) as well as drinking water and soil systems [49,51]. The key enzyme that mediates the conversion of nitrite to nitrate via NOB is NXR in *Nitrobacter* and the nitrite-oxidizing system in *Nitrococcus*, *Nitrospina*, and *Nitrospira.*

2.1.2. Process Technologies Used in Nitrification

Literature suggests the use of single-stage process in a reactor for nitrification technologies with a 200,000 m^3/day step-fed activated sludge process [36,52–54]. Altering aeration patterns (varying of cycle frequency vs. continuous and low vs. high) to influence the N_2O emission/production during nitrification has been observed to be a key parameter in reactor setups [55–57]. Additionally, membrane-biofilm reactor (MBFR)/membrane-aerated biofilm reactor (MABR) is an effective technology for nitrogen removal from wastewater. This process diffuses gases (viz. O_2, H_2, and CH_4) that mediate as electron donors/acceptors through a hydrophobic and permeable membrane onto a biofilm that is colonizing on the surface of the membrane [58]. MABR can also be altered to lead to the formation of layered biofilm structures with oxygen-controlled systems.

2.2. Denitrification

Denitrification is the process whereby nitrate is converted to nitrogen gas as the end product. It is generally the subsequent step of nitrification and is mostly performed by heterotrophic denitrifiers but can also be carried out by a limited number of autotrophic nitrifiers [5,59]. Various parameters play a major role in this process viz. maintenance of anoxic conditions, supply of carbon source, and subsequent treatment of the treated wastewater. The use of an external organic source of carbon is needed as external carbon can act as an electron donor needed for the growth of denitrifiers. The external sources of carbon include glucose, methanol, ethanol, succinate, and acetate [60,61]. The denitrification process of converting nitrate to nitrogen gas follows the following reaction [62]:

$$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 5CO_2 + 3H_2O + 4OH^- \quad (4)$$

where CH_2O represents an organic compound (carbon and energy source) and the denitrifiers use up nitrate instead of oxygen as electron acceptors. Denitrification often needs a posttreatment process, as the various external carbon sources often lead to turbidity (due to the presence of excessive biomass) in the treated water. Additionally, there is always a chance of the generation of the greenhouse gas nitrous oxide, which needs to be monitored [63].

2.2.1. Participation of Microorganisms in Denitrification

Microorganisms involved in this process include both autotrophic and heterotrophic bacteria, though the former is limited in number regarding its applicability than the latter. Additionally, the autotrophic bacteria display stunted growth and biomass generation with inefficient assimilation [64]. The working mechanism of autotrophic denitrifiers involves the oxidation of inorganic matter with the transport of discharged electrons to nitrate as a terminal acceptor. Rezvani et al. reported two types of autotrophic denitrifiers: hydrogen-based (*Micrococcus denitrificans* and *Paracoccus denitrificans)* and sulfur-based (*Thiobacillus denitrificans* and *T. thioparus*) [64]. In wastewater treatment processes, *Thiobacillus* sp. is the most widely observed autotrophic denitrifier [61].

Among the heterotrophic denitrifiers, the most widely observed are *Pseudomonas* and *Bacillus* [64]. These denitrifiers need strict anoxic conditions (with near-zero dissolved oxygen concentration of the wastewater), consume nitrate as the terminal electron acceptor, and harness the carbon from complex organic molecules. It has also been reported that these denitrifiers need smaller reactor volumes for effective bioconversion, thereby diminishing the cost factor associated with it. As reported in the literature, the most encountered denitrifiers in wastewater treatment units are members of the genera *Thauera, Paracoccus, Comamonas, Denitratisoma*, and the family Comamonadaceae [65–67].

2.2.2. Process Technologies Used in Denitrification

The various process technologies in denitrification include simultaneous nitrification and denitrification (SND) and shortcut nitrification and denitrification (SCND). The former is usually applied for wastewaters with a low C:N ratio (<5) where both nitrification and denitrification occur concomitantly in an anoxic environment [68]. SND function via both physical as well as biological methods. The former functions on the principle of the gradient of dissolved oxygen in the chamber, with limited diffusion of oxygen through the developed biofilm. Here, the nitrifiers confine themselves to areas having dissolved oxygen in the range of 1–2 mg/L, whereas the denitrifiers aggregate in the strata of low dissolved oxygen (<0.5 mg/L) [69,70]. In SCND, nitrification produces nitrite as the intermediate product, which is subsequently converted to nitrogen gas by nitrite denitrification [69]. The primary benefit of this process over conventionally used processes is that oxygen and electron donors are required less in the aerobic (25% less) and anoxic (40% less) stages, respectively [71].

2.3. Anammox

Anammox or anaerobic ammonium oxidation is a recently studied energy-efficient nitrogen removal process that is gaining popularity. In this process, nitrite and ammonium are used up, resulting in the formation of nitrogen gas along with NO and N_2H_4 intermediates (Equation (5)). In other words, it is the denitrification of nitrite, with ammonia acting as an electron donor. The nitrite can be gained from the oxidation of ammonium (nitrification) as well as partial denitrification of nitrate. Additionally, the anammox bacteria metabolize by using CO_2 as their only source of carbon and nitrite as an electron donor (Equation (6)) [7]. The nitrification/denitrification can consume up to 100% of the organic content of the wastewater. Nitrification/anammox can produce methane gas which can aid in bioenergy recovery from wastewater treatment [72]. The first full-fledged anammox reactor was established for the treatment of reject water in Rotterdam, Netherlands, and has ever since gained wide popularity and application [30].

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \quad (5)$$

$$CO_2 + 2NO_2^- + H_2O \rightarrow CH_2O + 2NO_3^- \quad (6)$$

2.3.1. Participation of Microorganisms in Anammox

Anammox bacteria possess a distinct modus operandi for survival: they consume ammonia when oxygen is unavailable. The most prolific group of bacteria that plays a key role in this process is *Planctomycete.* It thrives in freshwater, seawater as well as in terrestrial environments where anammox occurs. Apart from this, other characteristic anammox bacteria include *Brocadia anammoxidans* and *Kuenenia stuttgartiensis* [73]. According to Rahimi et al., around nineteen species and largely six genera of anammox bacteria have been widely studied and identified [30]. Additionally, van Niftrik and Jetten reported the enrichment of four genera viz. *Candidatus brocardia*, Ca. *kuenenia*, Ca. *anammoxoglobus, and* Ca. *jettenia* from natural marine ecosystems [74]. Though researchers have not been able to detect the presence of pure culture among the anammox bacteria, nonetheless, studies have successfully endeavored to enrich anammox culture as monospecies (like Ca. *scalindua)* under controlled conditions [75].

2.3.2. Process Technologies Used in Anammox

Anammox processes were first reported by Mulder et al. when employing a denitrifying fluidized bed reactor to treat the wastewater generated from a methanogenic reactor [76]. Broda had also outlined two thermodynamically probable molar ratios of ammonium and nitrite (1:1 and 1:1.67) for the oxidation of ammonia under a limited supply of oxygen [77]. However, as various studies from the literature have reported, this stoichiometry can also range from 0.5 to 4 in accordance with varying functioning conditions and reactor technologies employed [78,79].

Recently studied anammox process technologies include SNAD (simultaneous partial nitrification, anammox, and denitrification) and DEAMOX (denitrifying ammonium oxidation). SNAD process works for the concomitant removal of organic carbon along with inorganic nitrogen. Chen et al. had reported that SNAD operates by employing three bacterial communities viz. aerobic AOB, anammox, and denitrifying bacteria inside a single-reactor unit under scarce oxygen availability [80]. On the other hand, DEAMOX operates as a combination of anammox with partial denitrification by treating ammonia and nitrate-containing effluents. These two processes working in tandem result in high nitrogen removal rates (93.6%), irrespective of variation of ambient temperatures [81]. This process has many economic and technological advantages over other processes as well, such as low production of sludge and its subsequent management, decreased aeration and organic carbon requirement, and a substantial decrease in the emission of greenhouse gases (CO_2 and N_2O) [82].

3. Bioelectrochemical Systems

Apart from the conventional biological methods of nitrogen removal from wastewater, there is an increased interest currently in the various innovative bioelectrochemical alternatives. Such systems directly convert chemical energy present in the chemical bonds of the organic matter into electricity via electrochemically active bacteria (EAB), e.g., electricigens, and have potential applications for simultaneous nitrogen and other contaminants removal from wastewater with bioenergy recovery [22,23]. Here, the electrons are shifted to the anode after the oxidation of the pollutants, thereby removing them due to organic matter decomposition. Bioelectrochemical systems can be of two major types, conditional on the cathodic reaction: microbial fuel cells (MFCs; Figure 1A) and microbial electrolysis cells (MECs; Figure 1B). The former generates electrical power as the anodic oxidation works in tandem with cathodic reduction where electron acceptors with high reduction potential get reduced. The latter needs an externally supplied voltage (>0.2 V) under a biologically conducive environment, where EAB oxidizes the organic matter to produce CO_2, electrons, and protons. Subsequently, the EAB transfer the electrons to the anode and release the protons to the wastewater getting treated. When acetate is used as a substrate, the electrode reactions occurring are as follows [83,84]:

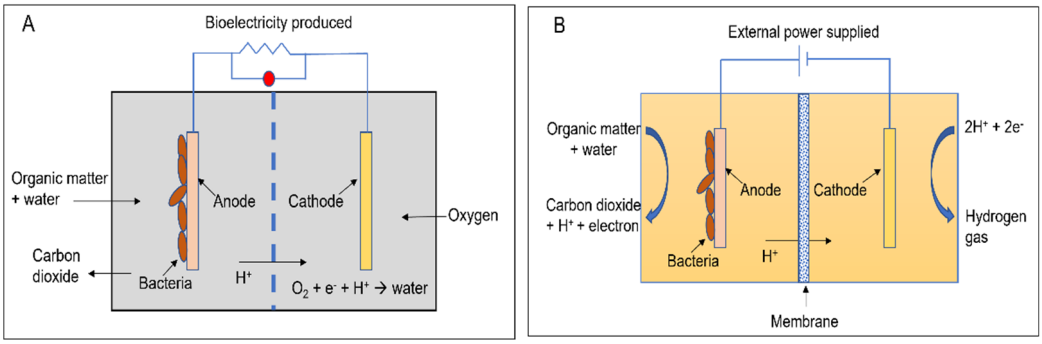

Figure 1. A two-chambered (**A**) microbial fuel cell and (**B**) microbial electrolysis cell.

For MFC-

$$\text{Anodic reaction: } CH_3COO^- + H_2 \rightarrow 2CO_2 + 2H^+ + 8e^- \quad (7)$$

$$\text{Cathodic reaction: } O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad (8)$$

For MEC-

$$\text{Anodic reaction: } CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8e^- + 8H^+ \quad (9)$$

$$\text{Cathodic reaction: } 8H^+ + 8e^- \rightarrow 4H_2 \quad (10)$$

Denitrification by bioelectrochemical systems can be performed in the cathodic chamber of the cells. Here, EAB in the anode oxidizes the substrate (like acetate) and supplies electrons which are utilized by the EAB at the cathode to perform denitrification. A tubular reactor MFC designed by Clauwaert et al. used acetate as an electron donor to perform denitrification with simultaneous bioelectricity production. The stepwise nitrate reduction reactions in this denitrification process are as follows [85]:

$$NO_3^- + 2e^- + 2H^+ \rightarrow NO_2^- + H_2O \quad (11)$$

$$NO_2^- + e^- + 2H^+ \rightarrow NO + H_2O \quad (12)$$

$$NO + e^- + H^+ \rightarrow 0.5N_2O + 0.5H_2 \quad (13)$$

$$0.5N_2O + e^- + H^+ \rightarrow 0.5N_2 + 0.5H_2O \quad (14)$$

$$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O \quad (15)$$

Zhao et al. had studied the performance of denitrifying MFCs with nitrite as an electron acceptor in the cathode with successful nitrite and total nitrogen removal [86]. They had also observed the predominance of the phylum *Proteobacteria* (35.72%) along with *Thiobacillus*, *Afipia*, and *Devosia*. Additionally, Zhu et al. and Zekker et al. had reported the occurrence of simultaneous nitrification-denitrification and anammox-denitrification, respectively, in MFCs to enhance the removal of nitrogenous contaminants from wastewater with concomitant and enhanced bioelectricity recovery [87,88]. Nitrogen removal by bioelectrochemical systems offers various benefits like diminished environmental impact, ability to remove specific pollutants, relatively inexpensive operating factors etc. Nonetheless, this being a novel process, we are still understanding the microbial kinetics and extracellular activities of the EAB, and further research in the context of engineering design and biotechnology will lead to more effectiveness.

4. Other Treatment Processes for Nitrogen Removal

Apart from the conventional biological and the novel bioelectrochemical processes discussed above, researchers are now studying other innovative microbial potentials as well. This has become possible due to the ushering of new findings that the conversion of

ammonium from wastewater to dinitrogen gas does not demand the absolute oxidation to nitrate that is consequently succeeded by heterotrophic denitrification. The following are a few such processes that explore the microbial abilities of the bacterial communities that can occur even during incomplete/partial oxidation of ammonium to nitrogen gas.

4.1. NO_x Process

During the NO_x process, the denitrification activity of bacteria similar to *Nitrosomonas* is controlled and stimulated by the addition of trace amounts of nitrogen oxides. The ratios of ammonium to nitrogen oxide that are added range from 1000:1 to 5000:1 [89,90]. With NO_x supply under completely oxic conditions, the *Nitrosomonas*-like bacteria can nitrify as well as denitrify concomitantly, with N_2 being the primary product. This process brings about 40% conversion of the ammonia present to nitrite and decreases the oxygen demand during the nitrification process by 50% with succeeding denitrification consuming less COD [7]. This is because here nitrite acts as the terminal electron acceptor to complete the process. The integrated nitrification-denitrification steps without NO_x supply are represented below by Equations (16)–(18) and that with NO_x supply by Equations (19)–(21). Here, the [H] denotes the reducing equivalents as provided by the external C-source. However, the stoichiometry and results might be influenced by the composition of the wastewater studied [91].

Conventional reactions:

$$\text{Nitrification: } 3NH_4^+ + 6O_2 \rightarrow 3NO_3^- + 6H^+ + 3H_2O \quad (16)$$

$$\text{Denitrification: } 3NO_3^- + 3H^+ + 15[H] \rightarrow 1.5N_2 + 9H_2O \quad (17)$$

$$\text{Total: } 3NH_4^+ + 6O_2 + 15[H] \rightarrow 1.5N_2 + 3H^+ + 12H_2O \quad (18)$$

Reactions with NO_x supply:

$$\text{Nitrification: } 3NH_4^+ + 3O_2 \rightarrow N_2 + NO_2^- + 4H^+ + 4H_2O \quad (19)$$

$$\text{Denitrification: } NO_2^- + H^+ + 3[H] \rightarrow 0.5N_2 + 2H_2O \quad (20)$$

$$\text{Total: } 3NH_4^+ + 3O_2 + 3[H] \rightarrow 1.5N_2 + 3H^+ + 6H_2O \quad (21)$$

4.2. Completely Autotrophic Nitrogen Removal over Nitrite (CANON)

The CANON process is an integration of partial nitrification and anammox processes [92–94]. The name of this process derives from the sequential working mechanism of the two sets of bacterial communities in a single and aerated reactor: *Nitrosomonas*-like aerobic and *Planctomycete*-like anaerobic bacteria (Equations (22) to (24)). These bacteria work in tandem to oxidize ammonia to nitrite (by nitrifiers), thereby consuming oxygen and subsequently creating an anoxic environment for anammox to proceed. This process is relatively sensitive to operational parameters viz. dissolved oxygen, the thickness of the biofilm developed, temperature, and loading rates of nitrogen [95]. This process has the economic advantage of requiring only a single reactor for operation.

$$NH_4^+ + 0.75O_2 + HCO_3^- \rightarrow 0.5NH_4^+ + 0.5NO_2^- + CO_2 + 1.5H_2O \quad (22)$$

$$NH_4^+ + 1.32NO_2^- + 0.066HCO_3^- + 0.13H^+ \rightarrow 0.066CH_2O_{0.5}N_{0.15} + 1.02N_2 + 0.26NO_3^- + 2.03H_2O \quad (23)$$

$$NH_4^+ + 0.85O_2 \rightarrow 0.44N_2 + 0.11NO_3^- + 1.43H_2O + 0.14H^+ \quad (24)$$

4.3. Single-Reactor High-Activity Ammonium Removal over Nitrite (SHARON)

The SHARON process is a type of partial nitrification process that was initially conceptualized for ammonia removal by the nitrite path [96,97]. Here, both autotrophic nitrification and heterotrophic denitrification occur simultaneously in one SHARON reactor with sporadic aeration. This process is however not conducive for all types of wastewaters

as it requires high temperature and works well for the elimination of high ammonium concentration (>0.5 g/L). Additionally, methanol needs to be added during the denitrification step of this process to better regulate pH and alkalinity production, required to balance the acidifying consequence of nitrification step. Equations (25)–(27) represent the stoichiometry of this process [7]:

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+ \quad (25)$$

$$2NO_2^- + 4.8\ g\ COD + 2H^+ \rightarrow N_2 + 1.8\ g\ sludge \quad (26)$$

$$2NH_4^+ + 3O_2 + 4.8\ g\ COD \rightarrow N_2 + 2H^+ + 1.8\ g\ sludge \quad (27)$$

4.4. Oxygen-Limited Autotrophic Nitrification and Denitrification (OLAND)

The OLAND process has been upheld by researchers as a one-step removal of ammonium without any supply of COD [98]. Though it is widely accepted that *Nitrifiers* are the responsible microorganisms in this process, nonetheless, studies are still being conducted to completely comprehend the mechanisms involved. Nevertheless, it appears to be based on either the CANON concept or the NO_x process, i.e., the functioning of aerobic and anaerobic ammonia oxidizers or that of nitrifying denitrifiers with NO_x being available [91]. Here, both the conversion efficiency and nitrogen loading rates are quite stunted [31,99]. The OLAND process has been represented by the following reactions [7]:

$$0.5NH_4^+ + 0.75O_2 \rightarrow 0.5NO_2^- + 0.5H_2O + H^+ \quad (28)$$

$$0.5NH_4^+ + 0.5NO_2^- \rightarrow 0.5N_2 + 2H_2O \quad (29)$$

$$NH_4^+ + 0.75O_2 \rightarrow 0.5N_2 + 1.5H_2O + H^+ \quad (30)$$

4.5. Aerobic Deammonification

Aerobic deammonification is yet another single-step process of ammonium removal that is independent of COD supply. In this process, a part of the ammonium is converted to dinitrogen gas and another part to nitrate [91,100]. This process majorly works on the concept of CANON mechanism, where nitrifiers and anaerobic ammonia oxidizers collaborate under limited oxygen supply. However, the nitrogen loading, as well as removal rates, are stunted here. The following reactions illustrate the aerobic deammonification process:

$$NH_3 + O_2 \rightarrow NH_2OH + H_2O \rightarrow HNO_2 \quad (31)$$

$$HNO_2 \rightarrow 0.33N_2 + 1.33H_2O + 0.33NO_2^- \quad (32)$$

$$NH_3 + O_2 \rightarrow 0.33N_2 + 1.33H_2O + 0.33NO_2^- \quad (33)$$

5. Processes of Nitrogen Recovery

Nitrogen is one of the most important building blocks of the formation of proteins and DNA. Though we have an abundance of gaseous nitrogen in the atmosphere, yet except for some bacteria, it cannot be utilized by most living organisms. To be utilized and to cater to the growing global human population in the form of fertilizers, it is imperative for nitrogen to be converted into its reactive forms such as ammonia, nitrate, nitrite, and ammonium. This is where recovery of nitrogen from wastewater can play an effective role to support agriculture as well as render wastewater fit for surface discharge at the end of the line to be reused as reclaimed water. In the following sections, nitrogen recovery by biological as well as chemical methods has been discussed.

5.1. Nitrogen Recovery by Microalgae and Cyanobacteria

Microalgae and cyanobacteria are potent alternatives for the biological treatment of wastewater with subsequent nitrogen recovery. As illustrated in Figure 2, microalgae and cyanobacteria photosynthetically produce O_2 during the treatment of nutrient-rich wastewater. This generated O_2 is subsequently used up by bacteria to disintegrate the

organic matter present in wastewater into simpler inorganic molecules [101,102]. These inorganic contaminants are subsequently eliminated during the tertiary treatment stage of wastewater treatment by the microalgae and bacteria so that the treated water can be safely discharged. These microalgae and bacteria assimilate nitrate and ammonia, which further get converted to biomass rather than being released to the environment in the form of gaseous nitrogen by the process of dissimilatory nitrate reduction. Cyanobacteria and microalgae do not possess structural carbon (such as cellulose; with C:N = 5 to 20), which renders them more competent in wastewater treatment and higher biomass production compared to complex plants (C:N = 18 to 120) [11]. For optimum performance of microalgae and cyanobacteria in this process, various parameters such as pH, temperature, light, etc., require control and monitoring [11,12,103]. The microalgal biomass generated from this process can be utilized to produce fertilizer, bioenergy, animal feed, pharmaceutical products, etc.

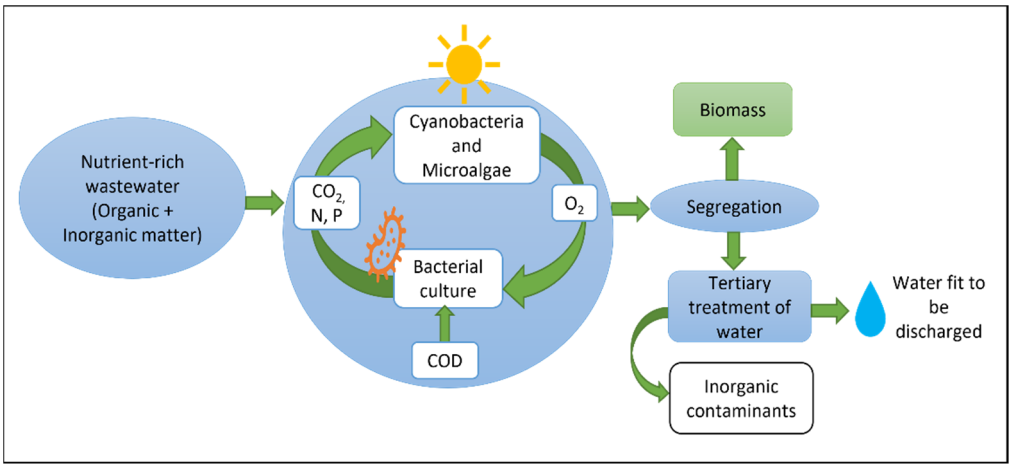

Figure 2. Nitrogen recovery from wastewater using microalgae and cyanobacteria.

5.2. Nitrogen Recovery by Chemical Processes

5.2.1. Struvite Precipitation

Struvite precipitation is a widely applied chemical method of ammonia and phosphorous removal from wastewater along with the associated environmental problems. This is a relatively simple yet effective and eco-friendly method of nitrogen recovery. The white crystalline mineral struvite ($MgNH_4PO_4 \cdot 6H_2O$) consists of equimolar ratios of Mg, NH_4, and PO_4. It is a potent slow-release fertilizer with a low level of contaminants that is poorly soluble in water and can substitute fertilizers [104]. This (Figure 3) process mainly occurs through the following reaction:

$$Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \quad (34)$$

This reaction is mainly impacted by two parameters viz. pH (basic pH of 9–10 is conducive) and the molar ratio of Mg:NH_4:P [82]. Escudero et al. reported that a molar ratio of 1:1:1 for Mg:NH_4:P can effectively remove 95% of NH_4^{+} from anaerobically treated wastewater in a timeframe of 30 sec [105]. Many researchers have studied the formation of struvite with subsequent ammonium recapture from treated wastewater (anaerobic), manure, urine, and industrial wastewater [106,107]. However, the disadvantage associated with this process is that, since the effluents are highly saturated with ammonia, they end up using large quantity of magnesium salts for effective precipitation. This ends up increasing the cost factor, thus stunting its large-scale application in many cases. Nonetheless, many studies have also suggested a multistage chemical method of integrating struvite precipitation with ammonia stripping (which is discussed below in Section 5.2.2) for successful ammonia removal along with other contaminants like COD and phosphorous [82].

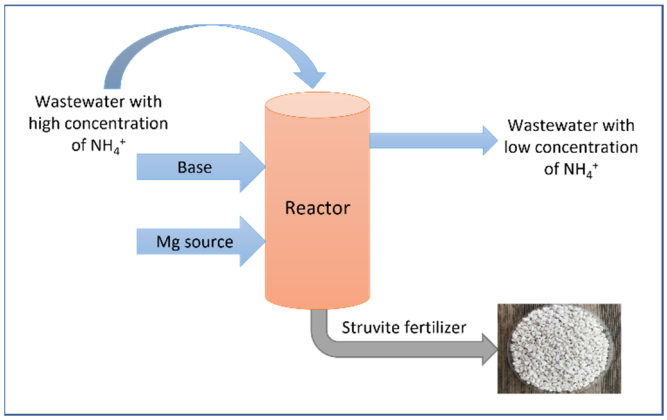

Figure 3. Nitrogen recovery by struvite precipitation.

5.2.2. Stripping Process

Stripping is a chemical method of removing ammonia by creating an environment thereby NH_4^+ gets converted to NH_3. Here, air or any other gas is forced through the wastewater so that NH_3 is rendered into the gas phase based on the process of desorption. The majority of the wastewaters contain ammonia or nitrogen-containing compounds in abundance. Further, as widely accepted, nitrogen removal from wastewater in the form of ammonia has lesser economic hindrances than that of other forms of nitrogenous species [108]. The concept behind this process is that NH_3 being a weak base, reacts with water (a weak acid) to generate NH_4OH (in the form of ions), which get converted to ammonia gas with the addition of lime or caustic (which shoots up the pH to 10.8 or 11.5). The NH_4^+ from the effluents can also be eliminated from the aqueous solution by steam or in the form of biogas [109]. Thus, the four key steps of its working are: (a) conversion of NH_4^+ to NH_3 (g); (b) diffusion of NH_3 to the borderline of air-water; (c) release of the formed NH_3 to the air–water interface; and (d) subsequent diffusion of NH_3 to the environment. Two types of ammonia stripping towers viz. cross-flow and countercurrent (as illustrated in Figure 4). The working mechanism of the cross-flow tower involves the flow of gas (air) along with the total depth of fill, as the alkaline wastewater streams downwards. Whereas, in the countercurrent tower, the air is introduced through the bottom while the wastewater is propelled to the top of the tower. Consequently, the stripping of free ammonia from the falling water droplets into the air stream occurs, which is then released into the atmosphere [110].

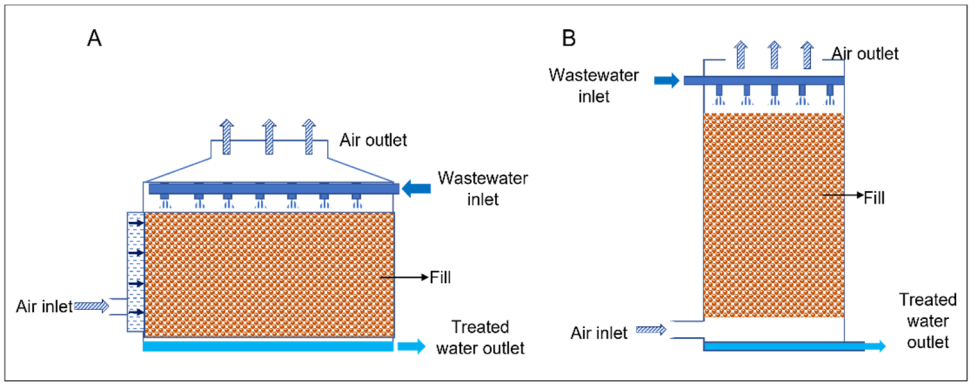

Figure 4. (**A**) Cross-flow and (**B**) countercurrent ammonia stripping towers.

To minimize the greenhouse effect the released NH_3 can cause, it can also be absorbed into phosphorous acid or sulfuric acid (as ammonium sulfate) [111]. However, this process finds the widest range of applications for nitrogen recovery in the form of fertilizer (40–60% ammonium sulfate solution with diminished organic contamination) [112]. This

process has the potential to aid agriculture in many areas by providing the necessary fertilizer input. Additionally, this process is not highly sensitive to pH and air temperature variation with no necessity for backwash or regeneration. Nonetheless, only NH_4^+ can be stripped by this technology with little effect on nitrite, COD, or phosphorous elimination from the wastewater [82].

5.2.3. Nitrogen Recovery Using Zeolite

Zeolites are compounds of hydrated aluminosilicates with SiO_4 and AlO_4 forming a 3-D tetrahedral network that is bridged by joint oxygen atoms. The partial substitution of Al^{3+} and Si^{4+} leads to the surplus negative surface charge offset by alkali and alkaline earth cations. These resulting cations located inside the tetrahedral network permit zeolite to exchange ions efficiently and function as an adsorbent resin in the ion exchange process. This principle is efficiently exploited during the removal of ammonium (and to some extent nitrate) [113]. Various researchers have studied the internal porosity, surface charge, cation exchange capacity (CEC), surface area and other such physicochemical features of zeolite that enable it to effectively carry out water remediation as well as act as agricultural fertilizers with eventual release of the nutrients (specifically NH_4^+, K^+, etc.) [114,115]. Specifically, after the release of ammonium ions, NH_3 can be thermally recovered from zeolite. Recently, increased focus is on integrated zeolite-anammox process for the removal of ammonium and nitrate without the need of substrate regeneration from the primary effluent of WWTPs [116,117]. However, this study has been mostly limited to university or research institute labs, and further study is needed to fully exploit this integrated system at full-scale domestic level.

6. Conclusions

The conventional processes of biological removal of nitrogenous entities from wastewater embraced mainly nitrification and denitrification. However, the discovery and applicability of the anammox process enhanced our comprehension of the nitrogen cycle and aided in utilizing the anammox microorganisms for the removal of nitrogen from wastewater highly saturated with ammonium. Further, the research and subsequent use of other nitrogen removal processes like NO_x, CANON, SHARON, OLAND, and aerobic deammonification with their combinations opened new vistas with enhanced removal efficiencies in wastewater treatment. Currently, the bioelectrochemical processes are very promising alternatives in the wake of climate change and environmental sustainability. However, these too face challenges in the context of scaling up with power generation that still needs to be enhanced. Additionally, further research is needed in the domain of reaction control, ease of electron shuttle via EAB, and materials used as electrodes. In a nutshell, considering the many attributes of the various processes discussed in this study, it often appears that their applicability cannot be generalized and is case-specific depending on the end use.

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