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Review

Advances in Nitrogen-Rich Wastewater Treatment: A Comprehensive Review of Modern Technologies

Abdullah Omar [1], Fares Almomani [1,*], Hazim Qiblawey [1] and Kashif Rasool [2]

[1] Chemical Engineering Department, Qatar University, Doha P.O. Box 2713, Qatar; ao1604980@qu.edu.qa (A.O.); hazim@qu.edu.qa (H.Q.)
[2] Qatar Environment and Energy Research Institute (QEERI), Hamad Bin Khalifa University, Qatar Foundation, Doha P.O. Box 34110, Qatar; krasool@hbku.edu.qa
* Correspondence: falmomani@qu.edu.qa

Abstract: Nitrogen-rich wastewater is a major environmental issue that requires proper treatment before disposal. This comprehensive overview covers biological, physical, and chemical nitrogen removal methods. Simultaneous nitrification–denitrification (SND) is most effective in saline water when utilizing both aerobic and anoxic conditions with diverse microbial populations for nitrogen removal. Coupling anammox with denitrification could increase removal rates and reduce energy demand. Suspended growth bioreactors effectively treated diverse COD/N ratios and demonstrated resilience to low C/N ratios. Moving biofilm bioreactors exhibit reduced mortality rates, enhanced sludge–liquid separation, increased treatment efficiency, and stronger biological structures. SND studies show ≥90% total nitrogen removal efficiency (%RE_{TN}) in diverse setups, with Defluviicoccus, Nitrosomonas, and Nitrospira as the main microbial communities, while anammox–denitrification achieved a %RE_{TN} of 77%. Systems using polyvinyl alcohol/sodium alginate as a growth medium showed a %$RE_{TN} \geq 75\%$. Air-lift reflux configurations exhibited high %RE_{TN} and %RE_{NH4}, reducing costs and minimizing sludge formation. Microwave pretreatment and high-frequency electric fields could be used to improve the %RE_{NH4}. Adsorption/ion exchange, membrane distillation, ultrafiltration, and nanofiltration exhibit promise in industrial wastewater treatment. AOPs and sulfate-based oxidants effectively eliminate nitrogen compounds from industrial wastewater. Tailoring proposed treatments for cost-effective nitrogen removal, optimizing microbial interactions, and analyzing the techno-economics of emerging technologies are crucial.

Keywords: wastewater treatment; nitrogen removal; microbial consortia; biocarrier materials; techno-economic analysis

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1. Introduction

Nitrogen plays a vital role in nature, serving various functions, with one of its most crucial roles being that of a primary component of proteins in living cells. While constituting 78% of the atmosphere in its elemental gaseous form (N_2), nitrogen takes on other forms, such as amino nitrogen in proteins and ammonia molecules consumed by plants and algae. The Nitrogen Cycle facilitates the movement of nitrogen in different environmental spheres. In its gaseous state, N_2 is highly stable and cannot be utilized directly. Bacteria play a pivotal role in fixing nitrogen through a complex series of interactions, starting with elemental nitrogen and culminating in the release of the ammonium ion (NH_4^+) during the decay of dead biomass. Lightning also contributes to nitrogen fixation in small concentrations. Synthetic fixation under extreme pressure and temperature using the Haber process can produce ammonia (NH_3) in the anthroposphere. Plants acquire nitrogen for growth and protein synthesis in the forms of NH_4^+ and NO_3^-. This nitrogen is sourced either from the natural bacterial fixation process or from synthetically manufactured fertilizers. Furthermore, NH_4^+ undergoes biological conversion to atmospheric nitrogen through a sequence of reactions involving oxidation and reduction of nitrogen atoms.

In the last few centuries, rapid technological advancements and population growth have resulted in elevated nitrogen levels in water and wastewater that pose threats to aquatic organisms and contribute to the degradation of freshwater, estuarine, and coastal marine ecosystems. Nutrient accumulation in water leads to the rapid proliferation of algae, forming an algal bloom that covers the entire water surface, obstructs sunlight penetration into the water, and contributes to a substantial mortality rate. Concurrently, a high nutrient concentration was connected to the surge in the growth of heterotrophic microorganisms that thrive on the deceased biomass, consuming oxygen and releasing carbon dioxide. Examples of algae blooms are common in Asia [1–3], Africa [4–6], Europe [7–10], and the Americas [11–16]. Considering the significant scale of this environmental issue and its profound impact on living organisms and humans, there has been and continues to be a focus on developing more effective methods for the removal of nitrogen from wastewater streams before discharge to the ecosystem. As a result, the effective removal of nitrogen from nitrogen-rich wastewater discharges is becoming an environmental priority.

It was reported that 300×10^3 m^3 of wastewater is generated annually, which was aligned with the development of wastewater treatment plants (WWTPs) worldwide to treat this high volume of water before release. The WWTPs are typically categorized into primary physical–chemical treatment and secondary biological treatment. The secondary effluents play a crucial role in the ecological replenishment of surface water bodies, but challenges arise as total nitrogen (TN) and total phosphorus (TP) often exceed standards. For example, certain wastewater streams, such as anaerobic digester effluents, landfill leachate, and industrial wastewaters, exhibit high ammonium concentrations. Conventional biological nitrogen removal processes, relying on nitrification–denitrification, face challenges in treating such ammonium-rich streams due to toxic effects on microorganisms and the need for external carbon sources. The threshold concentrations of TN and TP in aquatic environments causing eutrophication range from 0.5–1.2 mg/L and 0.03–0.1 mg/L, respectively. Despite firm environmental regulations in different countries, the effluent from most WWTPs still surpasses these limits, indicating inefficiency in TN and TP treatment capacities worldwide. Moreover, the characteristics of low C/N ratios in secondary effluent necessitate advanced nitrogen removal processes requiring additional carbon sources for biological denitrification, while chemical agents are often needed for advanced phosphorus removal. Tertiary treatment units are common in WWTPs for advanced nitrogen and phosphorus removal, employing technologies with high treatment costs and difficulties in simultaneous nitrogen and phosphorus removal. Emerging contaminants in the secondary effluent, such as PPCPs, antibiotics, microplastics, and other organic pollutants, have prompted the development of advanced treatment technologies. These include enhanced denitrifying phosphorus removal filters, pyrite-based autotrophic denitrification, and microalgae biological treatment systems, showing promise in laboratory and pilot studies for nitrogen and phosphorus removal from low C/N secondary effluent.

Our literature review analysis indicates that the current body of research on the treatment of nitrogen-rich wastewater has primarily concentrated on biological, physical, and chemical techniques. However, there is a significant lack of knowledge on the interactions involved in simultaneous nitrification–denitrification (SND) and anammox processes. Furthermore, there is a little research on the development of new technologies for advanced nitrogen and phosphorus removal from WWTPs' secondary effluent. Limited works have examined the techno-economics of advanced treatment processes for nitrogen removal to provide guidance for the actual application of emerging technologies in wastewater treatment. The interactions between microbial consortia with the objective to improve the efficiency of nitrogen removal in processes such as SND and anammox experienced limited modifications. Therefore, this literature review aims to fill that gap in knowledge by investigating the methods used to remove nitrogen compounds from wastewater. There are a wide variety of sources and components that must be considered while attempting to understand the complexity of nitrogen-rich wastewater treatment. To this goal, the research carefully explores the mechanics and operational complexities of the biological suspended growth and immobilized growth processes. At the same time, the effectiveness and application of physico-chemical removal techniques including air stripping, adsorption and ion exchange, and membrane and chemical treatments are carefully examined. Both adsorption and ion exchange techniques use solid materials as efficient capture agents, while air stripping enables the transfer of volatile nitrogen molecules into the gas phase. The research is innovative due to its focus on modern technologies such as membrane distillation, membrane-aerated biofilm reactors, and nanofiltration, which have superior capacities for removing ammonia. To remove nitrogen, membrane technologies use selective barriers, while chemical treatment processes require a wide range of chemical interactions. The outcome of this study will provide practitioners, academics, and policymakers working in the field of wastewater treatment useful insights into the latest technologies and an outline of their relative benefits and drawbacks. The study also discusses the contribution of novel configurations (e.g., air-lift reflux) and suggests combining ultrafiltration with membrane bioreactors for treating specific industrial wastewaters to achieve cost-effective technology that results in high nitrogen removal efficiency and less sludge production.

2. Characteristics of Wastewater

Wastewater can be classified as either domestic/municipal or industrial, though the line can be blurry for wastewaters coming from agricultural practices and landfill leachate. Studies showed that domestic wastewater is the most common form of wastewater [17–19]. This wastewater contains notable nitrogen and phosphorus compounds from household usage such as detergents. Agricultural wastewater has also been reported to include large amounts of N and P originating from fertilizers [20]. Moreover, industrial wastewaters from the energy production industry [21,22] and the metal industry [19,23] were reported to have high concentrations of nutrients. The concentrations of pollutants in these different types of wastewater have different ranges. For instance, food and swine wastewaters, unsurprisingly, contain large amounts of COD, $\geq$ 15,000 $\pm$ 3200 and 9000 $\pm$ 2100 mg/L, respectively [24]. The most important characteristics of wastewaters are summarized Table 1. The table offers a comprehensive overview of various wastewater types, delineating their chemical characteristics including chemical oxygen demand (COD) and nitrogen (N), phosphorus (P), and pH levels. Notable examples include biogas slurry from anaerobic reactors, exhibiting COD levels in the range 1220–1350 mg COD/L, nitrogen concentrations ranging from 575–620 mg-N/L, phosphorus levels between 30 and 42 mg TP/L, and a pH ranging from 7.5–8.5. Coking wastewater, on the other hand, contains 5231 $\pm$ 245 mg COD/L, 535 $\pm$ 29 mg TAN/L, and a pH of 8.1 $\pm$ 0.1. The diverse array of samples includes municipal wastewater, food waste digestate, landfill leachate, and semiconductor wastewater, each characterized by unique compositions and concentrations. This detailed breakdown underscores the necessity of tailoring wastewater management strategies to the specific contaminant profiles exhibited by various sources. It remains crucial to acknowledge that the definitive source is not the sole determinant of contaminants in wastewater. Factors such as geographical location, the nature of the industrial facility, population density, and even living standards and conditions, along with the economic status of a region, all exert significant influences—either directly or indirectly—on the characteristics of the wastewater produced.

Nitrogen (N) and phosphorus (P) are essential factors affecting water quality, playing a vital role in water body eutrophication. Nitrogen exists in various forms, including organic nitrogen, ammoniacal nitrogen (referred to as total ammonia nitrogen or TAN, encompassing NH_3-N and NH_4^+-N), and nitrite and nitrate ions (NO_2^--N, NO_3^--N). The combination of these nitrogen molecules is referred to as total nitrogen (TN) [25]. On the other hand, the term "total phosphorus" (TP) includes the compound phosphate (PO_4^{3-}), which is produced during the process of digestion. Maintenance of an optimal pH level is of utmost importance, especially in the context of bacterial growth, and it is an important role in numerous treatment procedures. A thorough understanding of the complexities associated with these characteristics is imperative for devising effective strategies in wastewater treatment. These intricacies will be rigorously examined in subsequent sections of this scholarly article.

Table 1. Typical reported relevant characteristics of wastewater from the literature.

Wastewater	COD (mg/L)	N (mg/L)	P (mg/L)	pH	Reference
Biogas slurry from anaerobic reactor	1220–1350	575–620 NH_4^+-N	30–42 TP	7.5–8.5	[21]
Coking wastewater	5231 ± 245	535 ± 29 TAN	-	8.1 ± 0.1	[22]
Domestic sewage wastewater	112.21–343.74	53.27–79.85 TN	4.46–6.90 TP	7.74–8.07	[18]
	-	168.87 NH_4^+	-	-	[26]
Domestic + blackwater wastewater	1000–3000	40–45 NH_4^+-N 46–62 TN	-	-	[27]
Food waste digestate	15,000 ± 3200	1600 ± 205 NH_4^+-N 2100 ± 300 TN	90 ± 15 PO_4^{3-} 125 ± 16 TP	7.8 ± 0.4	[24]
Landfill leachate	6693 ± 602	2564 ± 101 TN 2547 ± 270 NH_3-N	-	8.58 ± 0.18	[28]
	1537.50 ± 36.55	600.18 ± 16.18 NH_4^+-N 105.62 ± 3.84 NO_3^--N	-	8.03 ± 0.02	[29]
	1676	790 NH_3	-	-	[30]
Manganese electrolysis leachate	32 ± 3.0	823 ± 4.0 NH_4^+	3.0 ± 1.0 TP	4.0 ± 0.3	[19]
Municipal wastewater	-	61.04 NH_4^+ 70.19 TN	-	9.14	[31]
	-	15 NH_4^+-N	2 TP	-	[32]
	54 ± 5.7	0.006–26 NH_4^+-N	-	-	[33]
Semiconductor wastewater	-	25 NH_4^+-N	-	-	[34]
Sewage wastewater	53.79–116.04	5.54–17.35 NH_4^+-N 0.002–0.020 NO_2^--N 0.909–1.458 NO_3^--N	-	-	[17]
Space habitation wastewater	-	540–5100 TN	-	-	[35]
Swine wastewater	9000 ± 2100	700 ± 350 NH_4^+-N 1100 ± 225 TN	130 ± 18 PO_4^{3-} 160 ± 26 TP	7.2 ± 0.8	[24]
	27,131 ± 15,224	1308 ± 142 TAN	-	7.35 ± 0.19	[36]
	4105 ± 327	426 ± 21 TAN	103 ± 9.8 TOP	7.8 ± 0.1	[37]
	560	108 TAN	-	8.5	[38]
	1955 ± 622	575 ± 116 NH_4^+-N 688 ± 143 TN	-	-	[39]
	1009.50 ± 17.68	564.50 ± 7.07 TN 532.36 ± 5.24 NH_4^+-N	41.94 ± 0.41 TP	8.16 ± 0.11	[40]

Table 1. *Cont.*

Wastewater	COD (mg/L)	N (mg/L)	P (mg/L)	pH	Reference
Tungsten smelter wastewater	180–210	30–50 NH_4^+-N	1.5–1.8 TP	7–7.2	[23]
Urine wastewater (synthetic space ww)	-	565–1030 NH_4^+-N	-	8.37–8.77	[41]
Vanadium-extracted effluent	-	2850 ± 84 NH_4^+-N	-	2.5 ± 0.1	[42]

3. Biological Removal of Nitrogen

The microbial removal of nitrogen in the form of ammonium nitrogen (NH_4^+-N) from water bodies is a naturally observed process in which the ammonium ion is oxidized to nitrite (NO_2^-) by *Nitrosomonas* (Equation (1)), followed by further oxidation of nitrite to nitrate by *Nitrobacter* (Equation (2)) in a process called nitrification.

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+ \quad (1)$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \quad (2)$$

The described process depends on the availability of oxygen, thereby requiring aerobic conditions. In contrast to denitrification, an anoxic process entails the transformation of nitrate into elemental nitrogen by diverse bacterial species as a component of their metabolic activities. Nitrate can be released into the atmosphere as N_2, following Equation (3).

$$NO_3^- + C(food) \rightarrow N_2 + CO_2 + H_2O \quad (3)$$

Equations (1) and (2) make up the conventional treatment process known as the simultaneous nitrification–denitrification process (SND). While bacterial communities play a crucial role in both steps, algae can also contribute to the removal of ammonium ions by incorporating them into their biomass for growth and protein biosynthesis [43,44]. The feasibility of a bacteria–microalgae consortium for the removal of ammonia nitrogen in a photo-sequencing batch biofilm reactor has been studied by Li et al. [21]. This setup was used to treat biogas slurry wastewater from an anaerobic digestor. The results indicated that the symbiotic microalgae provided both oxygen and an extra organic carbon source for bacteria. The consortium demonstrated a $\%RE_{NH4}$ of 90% under reduced operational cost. The new process saved over 50% of the external carbon supply and lowered the oxygen demand by 78% compared to the traditional biological nitrogen removal process. Nitrogen was removed through short-cut nitrification–denitrification (SCND) (>80%) and biological assimilation (6.8%) in the PSBBR. The microbial community was later analyzed and found to be made of a diverse set of bacteria, although *Proteobacteria* showed the highest relative abundance (30–80%). Specifically, *Nitrosomonas* was identified for nitrification, and *Thauera* for denitrification. Nitrogen removal efficiencies higher than 90% were achieved, mostly owing to the nitrification–denitrification process performed by bacteria (>80%), but also due to bio-assimilation by microalgae (~7%). Moreover, microalgae reduced the oxygen and carbon demand in the system by 78% and 50%, respectively. Given that there is a clear symbiotic relationship between algae and bacteria, it is important to understand their behavior under different conditions. For example, the operation of a bacteria–algae consortium in a photo-sequencing batch biofilm reactor (PSBR) for the removal of nitrogen under continuous illumination should be compared with the process when it is operated with a 16 h/8 h light–dark cycle [45]. Although both processes showed an acceptable ammonium removal rate of 60 mg N/L/d and an excellent NH_4^+-N removal efficiency of 90–95%, continuous illumination showed higher biomass productivity. In addition, the light/dark cycle gave a higher denitrification rate (30 mg/L). The bacteria *Nitrosomonadaceae* were shown to have the highest abundance in the microbial community, and the green algae *Chlorophyta* was detected as well. Figure 1 summarizes typical pathways of biological nitrogen removal and involved bacteria [46].

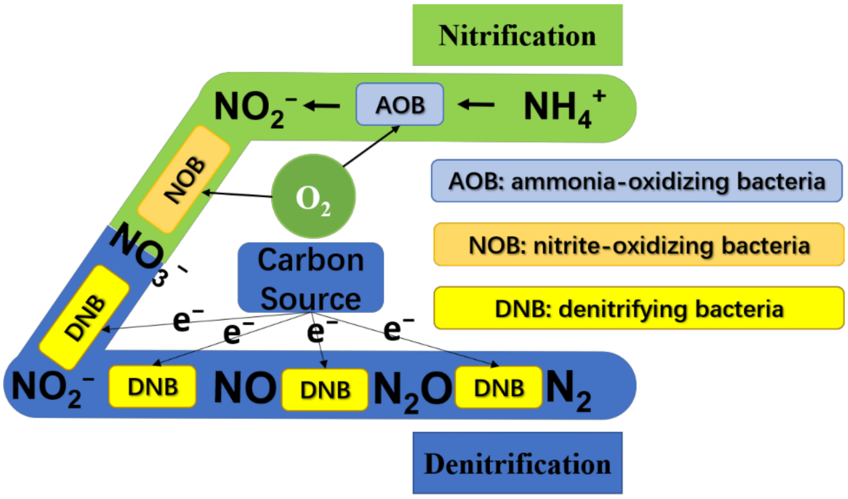

Figure 1. Typical pathways of biological nitrogen removal and involved bacteria [46].

Microalgae have attracted interest in recent years due to their distinctive metabolic properties, such as photosynthesis and effective nutrition digestion [47]. The features of microalgae make them very suitable for reducing nitrogen-related contamination in wastewater. In addition to providing an environmentally beneficial option, they also provide the potential for the utilization of biomass, generation of biofuels, and the simultaneous extraction of other nutrients [48,49]. Nitrogen uptake by microalgae primarily involves active transport, passive diffusion, and ion exchange processes. Microalgae effectively convert nitrogen-containing compounds into cellular biomass, thus offering a sustainable and natural method for removing nitrogen from wastewater [50]. The efficacy of microalgae in nitrogen removal depends on several parameters, including nutrition availability, light intensity, temperature, and pH [51]. Although the benefits of microalgae in nitrogen removal are clear, there are still obstacles to overcome, such as optimizing growth techniques and developing cost-effective methods for harvesting. A lot of research work exists on the utilization of microalgae for the remediation of nitrogen-rich wastewater. Thus, this part will outline the key findings about the utilization of algae for wastewater treatment. Su [52] provided a concise overview of the metabolic processes involving carbon, nitrogen, and phosphorus in microalgae. The study seeks to comprehend the nutrient absorption mechanisms in microalgae under varying operational situations. The importance of nutrients in cellular functions was emphasized, with carbon (C) providing the carbon skeleton, nitrogen (N) contributing to amino acid synthesis, and phosphorus (P) supporting ATP synthesis for energy-dependent processes. The minimum nutrient needs for 1 kg of microalgal biomass growth are 1.8 kg of carbon dioxide (CO2), 0.07 kg of nitrogen (N), and 0.008 kg of phosphorus (P). Municipal wastewater displays a range of C, N, and P ratios, with values varied from 100/0.6/0.6 to 100/193/12 (C:N:P). Additional forms of wastewater exhibit C:N ratios ranging from 875:1 to 0.85:1 and N:P ratios ranging from 20.98:1 to 0.12:1. The diverse components in wastewater and inconsistent ratios can significantly impact the performance of microalgae-based systems. In this context, Salbitani and Carfagna [53] conducted a comprehensive evaluation of previous research that focused on the removal of ammonium from wastewater using microalgae. The removal of ammonia often takes place during the tertiary stage of traditional wastewater treatment. Typically, a comprehensive and effective tertiary procedure, designed to eliminate TAN as well as phosphate from wastewater, tends to be more costly than primary treatment. The TAN fluctuates depending on the characteristics of the wastewater. The ammonium concentrations in municipal wastewater range from 27 to 100 mg/L [54,55]. Domestic wastewater, on the other hand, often shows levels between 39 and 60 mg/L [56]. Fish-processing wastewater has amounts ranging from 8 to 42 mg/L, highlighting the distinct pollutant profiles observed in different businesses. The ammonium concentrations in piggery wastewater vary significantly, ranging from 220 to 2945 mg/L. The ammonium contents in industrial-based effluent might vary from 5 to 1000 mg/L. Industries such as food processing, rubber processing, textile and leather manufacturing, fertilizer production, and agricultural and zootechnical sectors are known to emit significant amounts of ammonium. Concentrations of ammonium up to 100 mg/L typically originate from anaerobic digestion, when ammonium is generated by the breakdown of nitrogen-containing substances in the feedstock, mostly proteins. Our previous articles provide a thorough examination of the application, processes, and effectiveness of microalgae in removing nutrients from wastewater [48,57].

The potential of SND technology is boundless, with continuous research endeavors focused on enhancing its efficiency and cost-effectiveness. A promising avenue for advancing its performance lies in the cultivation of the microbial community integral to this technology. Ongoing efforts to refine and augment the capabilities of SND underscore its versatility and the constant pursuit of innovative solutions in wastewater treatment. The study revealed a substantial enhancement in the $\%RE_{TN}$ ranging from 19.8% to 46% when the community was facilitated by a graphene derivative. This represents a remarkable 125% increase in the $\%RE_{TN}$. Notably, under these conditions, the dominant bacterial genera were identified as *Bosea*, *Bacillus*, *Cupriavidus*, *Hydrogenophaga*, *Novosphingobium*, *Sulfurovum*, *Flavihumibacter*, and *Rhodovulum*. These findings underscore the impactful role of the graphene derivative in mediating community dynamics and fostering heightened nitrogen removal, shedding light on the key bacterial players that contribute to this improved efficiency. Luo et al. [23] explored the impact of salinity on the efficacy of the simultaneous nitrification–denitrification process within a membrane bioreactor. This investigation aimed to assess the feasibility of employing this process for the treatment of wastewater with elevated salinity levels [23]. It was noticed that up to 20% and 11% of $\%RE_{NH4}$ and $\%RE_{COD}$ could be removed during the salinity acclimation period. However, as salinity reached 3%, the SND efficiency reached 95.55%. The stoichiometry and kinetics of the system confirmed that increasing the salinity would significantly inhibit the electron transport system activity and the nitrification and denitrification processes.

Wastewater generated from a tungsten smelting facility underwent treatment by a microbial community led by *Chryseobacterium* in different salinity conditions. As salinity levels increased to approximately 3%, a shift in microbial dominance occurred, with *Nitrosomonas*, *Xanthomonas*, *Fusarium*, and *Belliella* emerging as the most influential genera. The initial rates of ammonium and COD removals were modest during the acclimation phase, registering at 20% and 11%, respectively. However, following the acclimation period at 3% salinity, the efficiency of the nitrification–denitrification reached 96%. This outcome underscores the practicality and viability of employing conventional nitrification–denitrification techniques for effectively treating wastewater characterized by elevated salt contents.

Mohammad and Fazaelipoor [58] showed that the mechanisms of SND in a fluidized bed biofilm reactor include complex interchanges between mass transfer and biochemical reactions [59]. The process illustrated in Figure 2 starts with the mass transfer of oxygen from the air to the liquid phase within the reactor. Oxygen is essential for the aerobic microorganisms present in the biofilm. Simultaneously, a mass transfer of substrates (COD and nitrogen species) from the bulk liquid phase to the surface of the biofilm occurs. Upon reaching the biofilm surface, these substrates diffuse within the biofilm structure. Within this biofilm environment, aerobic microorganisms utilize oxygen and organic carbon (COD) as energy sources to oxidize ammonium and nitrate, facilitating nitrification. Nitrite, an intermediate product of nitrification, is further denitrified by denitrifying bacteria in the presence of organic carbon and nitrate. This denitrification process converts nitrite and nitrate into nitrogen gas, which is released from the system. The governing equations for this model are based on the uniform coverage of solid particles by biofilm, constant biofilm thickness, multiple substrates, and Monod-type expressions for bioreaction rates within the biofilm. These assumptions provide the groundwork for understanding the intricate SND mechanism in the fluidized bed biofilm reactor. Importantly, this process underscores the crucial role of biofilm in facilitating simultaneous nitrification and denitrification, making SND an effective method for nitrogen removal from wastewater in engineered biological systems.

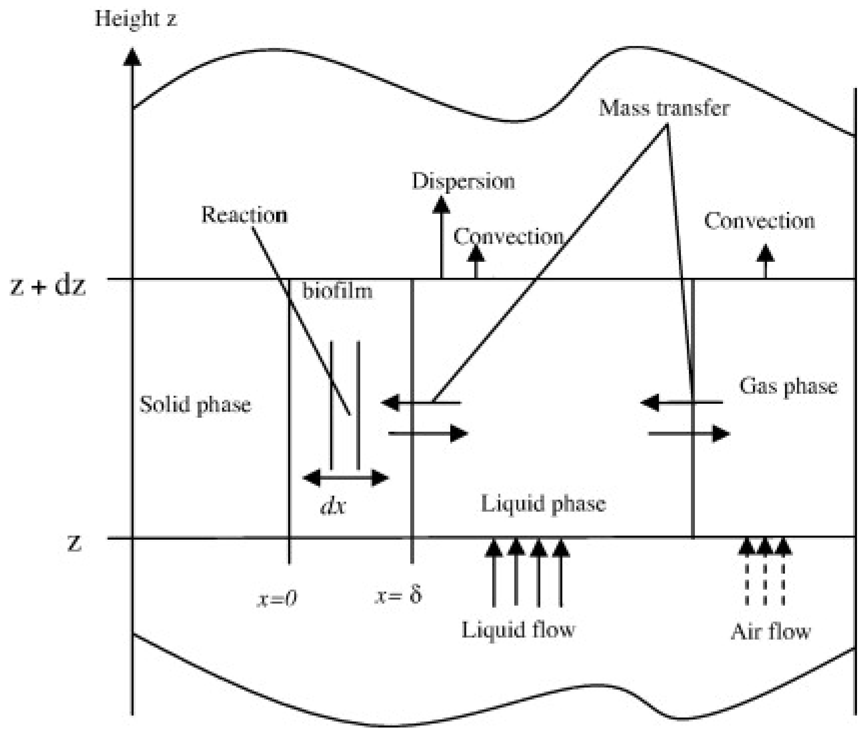

Figure 2. The mechanisms and the corresponding phases involved in a fluidized bed biofilm reactor [58]. Reprinted with permission from reference [58], License Number 56558201823.69.

One of the most interesting discoveries made in this century is the anammox process with the corresponding bacterial genera. The anammox (anaerobic ammonium oxidation) process, sometimes referred to as the short-cut biological nitrogen removal (SBNR) process, is like the conventional SND process, but without the second oxidation and denitrification steps. Certain bacteria of the phylum Planctomycetes directly convert ammonium and nitrite ions into N_2 as per Equation (4):

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \quad (4)$$

This process has the potential to save much energy and treatment cost since there is no need for the nitrification of nitrite to nitrate (oxygen demand) and denitrification of nitrate to nitrogen. Chen et al. have tested this potential by combining the conventional nitrification–denitrification process with the anammox process to enhance performance and lower the cost to treat raw digested swine wastewater [39]. The microbial community was later analyzed and found to be dominated by *Candidatus Brocadia* in the anammox section, and *Denitratisoma*, *Pseudomonas*, *Bacillus*, and *Thauera* in the denitrification section. This improved design increased the $\%RE_{TN}$ from 39 to 77% and reduced energy consumption by 50%. Further modification was proposed by combining short-cut nitrogen removal with phosphorus removal within an aerobic/anaerobic reactor. In such a configuration, sludge undergoes free nitrous acid (FNA) treatment to prevent polyphosphate accumulation [60]. The process was employed to treat synthetic wastewater, and the analysis of the microbial community showed a rapid increase in the abundance of *Comamonas* and *Tetrasphaera* in the post-FNA treatment. The reported removal efficiencies of NH_4^+-N ($\%RE_{NH4}$), PO_4^{3-}—P ($\%RE_{PO4}$), and $\%RE_{TN}$ were 100, 98, and 80%, respectively. However, when this process's economy was compared with conventional biological nitrogen removal and chemical phosphorus removal, the latter gave the highest savings per cost. On the other hand, Ritigala showed that the pretreatment of swine wastewater and food waste digestate by magnetic coagulation prior to SBNR has higher removal efficiencies [24]. The reported $\%RE_{NH4}$ and $\%RE_{NH4}$ were 97.30 ± 0.3% and 99.7 ± 0.2%, respectively, for swine wastewater and 97.44 ± 0.3% and 98.54 ± 0.2% for food waste digestate. The process was also shown to exhibit high removal rates of TSS (89–92%), COD (96–97%), and TP (88–92%). It was observed that the dominant microbial communities in these two wastewaters were *Nitrosomonas* for nitrification and *Diaphorobacter* and *Thauera* for denitrification.

The previous literature analysis highlights the effect of microbial communities on the removal of nitrogen compounds from wastewater, focusing on the natural process involving Nitrosomonas and Nitrobacter in the nitrification process. This process relies on aerobic conditions and contrasts with denitrification by various bacterial species under anoxic conditions. While bacteria such as Nitrosomonas and Thauera play pivotal roles in nitrogen fixation and removal, algae contribute to ammonium ion removal by assimilating it for growth and protein biosynthesis. The analysis emphasized the symbiotic relationship between bacteria and microalgae, leading to reduced oxygen and carbon source demands, while achieving high nitrogen removal efficiency. Furthermore, the simultaneous nitrification–denitrification process (SNDP) shows an excellent performance in removing nitrogen compounds from wastewater. The importance of incorporating different materials (e.g., graphene) in the microbial community for the subsequent improvement in nitrogen removal efficiency has been highlighted. The anammox process, an anaerobic ammonium oxidation mechanism, is another cheap and energy-efficient method for treating nitrogen-rich wastewater. Combining conventional nitrification–denitrification with anammox demonstrated increased removal efficiencies and reduced energy consumption. Table 2 presents key findings of the biological nitrogen processes.

Table 2. Key findings of the biological nitrogen processes.

Aspect	Findings/Highlights
Nitrification/Denitrification Processes	➢ Nitrification oxidation of ammonium to nitrite (NO_2^-) by Nitrosomonas and further processing to nitrate (NO_3^-) by Nitrobacter in nitrification process requires aerobic conditions. ➢ Denitrification is a process converting nitrate to elemental nitrogen.
Role of Bacterial Communities and Algae	➢ Bacterial communities (e.g., Nitrosomonas, Thauera) are vital for nitrification and denitrification. ➢ Algae contribute to ammonium ion removal by assimilation. ➢ Symbiotic bacteria–microalgae consortium demonstrated high efficiency in wastewater treatment. ➢ Bacteria–microalgae consortium reduced operational costs, providing oxygen and organic carbon for bacteria.
Simultaneous Nitrification–Denitrification (SND)	➢ SND technology shows versatility in nitrogen removal. ➢ Graphene derivative enhances $\%RE_{TN}$ efficiency by up to 1.25-fold. ➢ Dominant bacterial genera (e.g., Bosea, Bacillus) contribute to improved nitrogen removal. ➢ Symbiotic microbial communities play a crucial role in SND.
Anammox Process	➢ Anammox process converts ammonium and nitrite ions directly into N_2 without the need for denitrification. ➢ Offers potential energy and cost savings in wastewater treatment. ➢ Combining anammox with conventional nitrification–denitrification enhances performance and reduces costs. ➢ Microbial community analysis identifies key genera like Candidatus Brocadia in anammox.

Table 2. *Cont.*

Aspect	Findings/Highlights
Impact of Salinity on Nitrogen Removal	➢ Salinity influences the efficiency of simultaneous nitrification–denitrification. ➢ Up to 95.55% efficiency achieved with 3% salinity. ➢ Microbial community shifts observed in wastewater treatment at varying salinity levels.
Potential of SND Technology	➢ Continuous research aims to enhance SND efficiency and cost-effectiveness. ➢ Cultivation of microbial communities, facilitated by a graphene derivative, improves $\%RE_{TN}$. ➢ Diverse bacterial genera identified (e.g., Bosea, Bacillus) in enhanced SND.
Anammox Process and Cost-Efficiency	➢ Combination of conventional nitrification–denitrification with anammox increases removal efficiency. ➢ Reduced energy consumption observed. ➢ Microbial community analysis reveals dominant genera in the anammox section. ➢ Proposed design combining short-cut nitrogen removal with phosphorus removal shows promise in synthetic wastewater treatment.
Challenges in Microalgae Utilization	➢ Microalgae's distinctive properties make them suitable for wastewater nitrogen reduction. ➢ Challenges include optimizing growth techniques and developing cost-effective harvesting methods.

3.1. Suspended Growth

In suspended growth bioreactors, nitrogen-removing bacteria are not attached to any fixed material and can mix freely in the wastewater due to aeration. The advantages of such processes include simpler designs and lower costs, but due to the presence of large amounts of sludge in the effluents, the installation of secondary sedimentation tanks is required to recover and recycle microbial cultures. Xu et al. [61] investigated the removal of nitrogen in an integrated two-stage anoxic and aerobic activated sludge process treating landfill leachate. A 600 m^3 anoxic chamber followed by two 1700 m^3 and 600 m^3 aerobic tanks with recycle ratios of 9.6 and 18.24 were used in the first stage. The second stage includes a 300 m^3 anoxic and same-volume aerobic process. The recycle ratios in the first and second anoxic chambers were set at 10.08 and 4.32, respectively. The reported $\%RE_{TN}$ and $\%RE_{NH4}$ and NO_3^- and NO_2^- removal efficiencies were 97.6%, 99.1%, 100%, and 100%, respectively. Ninety percent of the $\%RE_{TN}$ was attributed to the primary stage, where nitrate and nitrite showed complete removal. The analysis of the microbial community showed a high abundance of *Defluviicoccus* genus compared to *Nitrosomonas* and *Nitrospira*, leading to the conclusion that most of the nitrogen removal occurred due to ammonia nitrogen assimilation by bacteria as a nutrient rather than the traditional nitrification–denitrification.

A standalone anaerobic suspended sludge continuous flow bioreactor has been reported to efficiently remove ammonia nitrogen. Xia et al. [62] suggest a novel approach to treat wastewater containing ammonium perchlorate (NH_4ClO_4) generated from the explosives and fireworks industries. Their innovative design involves coupling anammox in a 3.5 L reactor and sulfur-oxidizing microorganisms in a separate 2.5 L reactor. This integrated system, known as CAS, functions at a temperature of 30 °C, a hydraulic retention time (HRT) of 3.5 h, and a pH of 7.3. Oxygen is supplied to the second reactor as part of the operational setup. The anammox reactor alone achieved a $\%RE_{TN}$ of 85% when the synthetic influent contained 120 and 100 mg/L NO_2^--N and NH_4^+-N, respectively. The $\%RE_{TN}$ was further increased to 99% for the whole CAS system when ClO_4^- solute was added to the wastewater influent. This increase in process efficiency was attributed to the increase in the secretion of extracellular polymeric substances (EPSs) due to the ClO_4^- in the wastewater medium, suggesting the possibility of the simultaneous removal of the two pollutants because of this synergy. *Candidatus Kuenenia* was the dominant genus in the former reactor, while *Methyloversatilis*, *Thermogutta*, and *Longilinea* were so in the latter.

Although the activated sludge process is widely favored in modern treatment plants for its capacity to handle large volumes of wastewater, Sequencing Batch Reactors (SBRs) present a competitive advantage in terms of removal efficiencies. This is attributed to their unique ability to operate in various aerobic/anaerobic modes by regulating aeration within a single bioreactor. Such control facilitates the cultivation of a diverse microbial community capable of nitrification, denitrification, and aerobic/anaerobic ammonia oxidation. Consequently, this leads to increased biodiversity and enhanced overall performance. Kao et al. [63] integrated simultaneous nitrification–denitrification (SND), endogenous denitrification, and anaerobic ammonium oxidation (anammox) within a single bioreactor. The developed system facilitates the cultivation of all relevant microbial communities across various operational phases, specifically designed for the treatment of municipal wastewater. The 10 L bioreactor underwent alternating anaerobic, aerobic, and anoxic conditions for 2.5, 1.5, and 4 h, respectively, resulting in a total hydraulic retention time (HRT) of 8 h. The system was operated at temperatures ranging between 20 and 25 °C. The bioreactor operated through five distinct phases, each characterized by a different HRT. For instance, phase 1 extended from the initial setup until day 27. Remarkably, the reported $\%RE_{NH4}$ after 233 days of continuous operation in phase 5 reached 94%. During this period, the bioreactor received alternating feeds of 4 and 1 L of wastewater with a 4 h interval. Notably, anammox and denitrification bacteria played pivotal roles in $\%TN_{rem}$, contributing 79% and 21%, respectively, despite the former being less abundant than the latter. The dominant genera in the microbial community after 196 days were identified as *Candidatus Brocadia*, *Nitrospira*, and *Denitratisoma* which were almost non-existent at the beginning of cultivation, hence highlighting the appeal of SBRs. The concept of integrating anammox technology into the SND treatment of nitrogen-rich municipal wastewater was further investigated by Gao et al. [64], who employed a comparable experimental setup with some modifications. The operation of the 61 L chambers, encompassing anaerobic, aerobic, and anoxic processes, occurred at an HRT of 16 h and temperatures in the range 17 to 28 °C over 233 days. The bioreactor showed a good average %TIN and $\%RE_{NH4}$ of 85% and 93%, respectively. It was suggested that the remaining nitrogen in the effluent was due to excess ammonia and nitrate in the influent. Despite the decreasing temperature over time, there was an increase in the removal rates of nitrogen. This observation may have significant implications regarding the importance of microbial species in relation to general growth rate kinetics. The dominant bacteria in the bioreactor were *Candidatus Brocadia*, *Nitrospira*, and *Denitratisoma.* Compared to the previous work, glycogen-accumulating organisms (GAO) and phosphorus-accumulating organisms (PAO) *Candidatus Competibacter* and *Tetrasphaera* were identified at higher concentrations.

Testing of the feasibility of establishing highly diverse microbial cultures and integrating anammox, nitrification, and denitrification in Sequencing Batch Reactors (SBRs), and to a lesser extent, activated sludge processes, is essential. This evaluation is particularly crucial for low-organic substrate-to-nitrogen content-ratio (C/N) wastewaters. The lower concentrations of organic substrate may be considered a potential discouraging factor for microbial growth in such scenarios.

Wang et al. [65]. delved into an examination of the performance of an integrated combined SND–anammox suspended sludge bioreactor for municipal wastewater treatment, particularly focusing on its efficacy at extremely low C/N ratios. The study was conducted in a 10 L bioreactor operated at three distinct stages and under varied COD/N ratios, HRTs of 17–18 h, a temperature of 22 °C, and a pH of 7.5. The proposed treatment method not only exhibited tolerance but also a preference for very low COD/N wastewaters, achieving a remarkable $\%TR_{NH4}$ of 92% at a COD/N ratio of 1.9. Analysis of the mixed culture revealed a higher abundance of Candidatus Competibacter (GAO), Candidatus Brocadia (anammox), Tetrasphaera (PAO), and Denitratisoma (denitrification). In contrast, there was a smaller presence of nitrifying bacteria (partial nitrification) at higher ratios. These findings highlight the favorability of specific microbial populations over heterotrophic bacteria in low C/N conditions. Li et al. [66] conducted a thorough investigation into the effectiveness of employing a Bi-Bio-Selector for nitrogen and phosphorus removal (BBSNP) from municipal wastewater at low C/N ratios as compared to conventional anaerobic–anoxic–aerobic reactors (AAOs). The BBSNP process, while incurring slightly higher costs, offered the additional benefit of phosphorus removal. The process, with a total volume of 36 m^3, includes equal-volume anoxic/anaerobic/aerobic tanks. This is different from AAO, which featured a larger anoxic volume and reduced aerobic volume. The BBSNP process operated at an HRT of 9.36 h, a temperature of 15 °C, and a pH in the range 7.1 to 7.6 and achieved excellent treatment efficiency, with a $\%TN_{rem}$ and $\%TN_{NH4}$ of 83% and 99%, respectively, at a C/N ratio of 2. In comparison, an AAO exhibited a substantial decline in performance as the C/N ratio decreased, reaching 60% and 75% for $\%TN_{rem}$ and $\%TN_{NH4}$, respectively. Notably, the microbial analysis revealed the dominance of fermenting Saccharibacteria, followed by denitrifying phosphorus-accumulating Dokdonella, Tetrasphaera and Candidatus Microthrix, and the traditional denitrifying Ferruginibacter and Ottowia. In contrast, Nitrospira and Nitrosomonas were nearly non-existent in the system.

Cui et al. [67] investigated the contribution of the aerobic ammonia-oxidizing bacteria referred to as comammox in an anammox-dominated up-flow anaerobic sludge blanket (UASB) bioreactor for the treatment of low strength municipal wastewater. The USAB reactor had a working volume of 5 L, and it treated municipal sewage at an HRT of 3.7 h with a temperature and C/N ratio of 30 °C and 1.8, respectively. Following microbial acclimation under synthetic wastewater, municipal sewage was used as the influent, containing ammonia and nitrite as the nitrogen sources, and the resulting %TIN of 93% was achieved. The remaining nitrogen content existed in the form of NO_3^--N, which can be attributed to the nitrifying comammox *Nitrospira* strain that was observed to be more abundant than other nitrifiers. However, the bioreactor remained dominated by the anammox *Candidatus Brocadia* and *Candidatus Kuenenia* bacteria, hence, most of NH_4^+-N was converted to nitrogen. These findings were not compared to the performance of similar experimental setups without the addition of comammox bacteria, which makes it difficult to quantify their questionable contribution, but they are positive, nevertheless.

The defining feature of suspended growth bioreactors is the lack of a cohesive biofilm layer attached to a surface due to the EPSs that the microbial organisms produce in their growth process. While they are, therefore, easy to differentiate, some rare cases of innovation may prove otherwise, such as when there is an addition of microparticles for bacteria to attach to but a biofilm is not formed. Chen et al. [68] modified the traditional activated sludge process through the addition of magnetic PS@Fe_3O_4 microparticles that are suspended in the cultivation medium in a hybrid attached/suspended growth SBR. The Sequencing Batch Reactor, which has a volume of 500 mL, HRT of 11 h, temperature of 23 °C, and pH of 7, filled with 1.67% of microparticles, was used to test the efficiency in treating synthetic wastewater. It was observed that after only 3 weeks of operation, the $\%RE_{TN}$ and $\%RE_{NH4}$ reached 71% and 95%, respectively, in contrast to 48% and 88% for a traditional suspended activated sludge bioreactor operated at the same conditions. In addition to the superior performance, the enhanced culture showed variation in the microbial community, most notably a higher abundance of *SM1A02*, *Thauera*, *Dechoromonas*, and *Nitrosomonas*. This modification's attractiveness lies in its improved performance and in the facilitated separation made possible by the nature of the polystyrene composites in the sludge. This characteristic enables much easier sedimentation under the influence of a magnetic field. Table 3 summarizes recent literature regarding suspended growth nitrogen removal from wastewaters.

Suspended growth bioreactors have a more streamlined design that results in reduced treatment expenses. This system can function independently as a treatment procedure for eliminating ammonia nitrogen from wastewater with high levels of strength. Suspended growth bioreactors can combine several microorganisms, including sulfur-oxidizing bacteria, and simultaneous nitrification–denitrification (SND), endogenous denitrification, and anaerobic ammonium oxidation (anammox), to achieve the efficient removal of pollutants. These bioreactors exhibited resilience in relation to COD/N ratios. In addition, modified activated sludge can be achieved by introducing comammox bacteria into an anammox-dominated up-flow anaerobic sludge blanket (UASB) bioreactor, resulting in a significant total inorganic nitrogen (TIN) removal.

Table 3. Suspended growth bioreactors for treating nitrogen-rich wastewaters.

Process	Bioreactor	Influent Conc.	Removal Efficiency	Dominant Bacteria	Reference
Activated Sludge	V: 3500 m^3 HRT: 168 h	TN: 2885 mg/L NH_4^+-N: 2609 mg/L NO_3^--N: 7 mg/L NO_2^--N: 0.4 mg/L DON: 269 mg/L	TN: 98% NH_4^+-N: 99% NO_3^--N: 100% NO_2^--N: 100% DON: 83%	*Defluviicoccus*	[61]
	V: 6 L HRT: 3.5 h T: 30 °C pH: 7.3	NO_2^--N: 120 mg/L NH_4^+-N: 100 mg/L	TN: 99%	*Candidatus Kuenenia*	[62]
	V: 36 m^3 HRT: 9.4 h T: 15 °C pH: 7.4	TN: 31 mg/L NH_4^+-N: 21 mg/L	TN: 83% NH_4^+-N: 99%	*Saccharibacteria* *Ferruginibacter* *Dokdonella*	[66]
Sequencing Batch Reactor	V: 500 mL HRT: 11 h T: 23 °C pH: 7	TN: 60 mg/L NH_4^+-N: 60 mg/L	TN: 71% NH_4^+-N: 95%	*SM1A02* *Zoogloea* *Thauera*	[68]
	V: 10 L HRT: 16 h T: 23 °C	NH_4^+-N: 71 mg/L	NH_4^+-N: 94%	*Candidatus Brocadia* *Nitrospira* *Denitratisoma*	[63]
	V: 61 L HRT: 16 h T: 23 °C	TN: 67 mg/L NH_4^+-N: 67 mg/L	TN: 85% NH_4^+-N: 93%	*Candidatus Brocadia* *Nitrospira* *Denitratisoma*	[64]
	V: 10 L HRT: 17 h T: 22 °C pH: 7.5	NH_4^+-N: 75 mg/L	NH_4^+-N: 92%	*Candidatus Competibacter* *Tetrasphaera* *Norank OLB14*	[65]
Up-flow Sludge Blanket	V: 5L HRT: 3.7 h T: 30 °C	TN: 53 mg/L NH_4^+-N: 26 mg/L NO_2^--N: 27 mg/L	TN: 93%	*Candidatus Brocadia* *Candidatus Kuenenia* *Nitrospira*	[67]

3.2. Immobilized Growth

The work of Chen et al. [68] serves as a good introduction to the benefits of an immobilized growth system. Embedding microbial cultures onto high-surface-area protective materials (e.g., polymers) and fostering the development of a biofilm offer numerous benefits. These advantages include reduced mortality rates, complete segregation between biological sludge and the liquid phase, enhanced treatment efficiencies, and the creation of robust biological structures. This facilitates both aerobic and anaerobic growth concurrently, attributed to partial exposure to dissolved oxygen on the outer surface of the biofilm as opposed to the inner part, among various other advantages [69,70]. Furthermore, the management and transfer of microbial cultures are made more convenient for the cultivation and growth of cultures in other chambers for optimization purposes, thanks to the EPS matrix formed on the surface that effectively "sticks" the cells to the biocarriers. Table 4 summarizes the experimental results of the different immobilized growth technologies in recent years.

Moving bed biofilm reactors (MBBRs) represent the most prevalent type of immobilized cell bioreactors. In these systems, a biofilm develops on numerous distinct biocarriers, which are typically suspended in the wastewater medium through mixing and/or aeration [71–75]. Zhou et al. [76] explored the performance of a two-stage anoxic/oxic MBBR for the removal of nitrogen from the effluents of primary municipal wastewater. The initial phase comprised two anoxic reactors succeeded by three oxic chambers, whereas the subsequent stage included two anoxic and only one oxic chamber. The volume of each chamber was 0.7 m^3, operated at an HRT of 11.2 h and pH in the range of 6–8 pH, and the temperature varied from 15–27 °C. The biocarriers were filled at 40% and 50% of the anoxic and oxic tanks, respectively. The highest $\%TN_{rem}$ and $\%TN_{NH4}$ of 92% and 98% were achieved during the summer period, showing that moderate to high temperatures favored the nitrification–denitrification process. During the winter, a higher presence of nitrifying autotrophic bacteria was observed. Consequently, it is plausible that the diminished treatment efficiencies were a result of lower microbial activity during this season. The microbial community was dominated by *Nitrospira*, *Nitrosomonas*, *Hyphomicrobium*, *Rhodobacter*, and *Thermomonas* in the oxic chambers, while *Thauera*, *Arcobacter*, *Dechloromonas*, *Rhizobium*, *Sulfuritalea*, and *Denitratisoma* were abundant in the anoxic tanks. The design of the MBBR was further modified by Zhou et al. [77], who suggested a novel two-stage nitrification–denitrification process to enhance nitrogen removal from municipal wastewater. In this revised design, the influent is divided into two parallel streams. Each stream undergoes treatment in two anoxic chambers (1400 m^3) before being directed to two oxic chambers (1802 m^3). Subsequently, the treated streams merge and flow into a final anoxic chamber (750 m^3), followed by entry into the ultimate oxic chamber (233 m^3). The high-density polyethylene biocarriers were filled to 50% and 55% of the anoxic and oxic chambers, respectively. The system, which was operated at 20 °C, a pH of 7.5, and an HRT of 9.8 h achieved $\%RE_{NH4}$ and $\%RE_{TN}$ 99.11% and 74.03%, respectively; the latter was increased to 91.76% by the addition of external carbon sources. The anoxic tanks were found to have denitrifying *Methylotenera*, while the nitrifying *Nitrosomonas* and *Nitrobacter* were abundant in the oxic chambers. While this work boasts the advantage of being feasible on a large scale, questions arise about its effectiveness in eliminating TN. This skepticism arises because current traditional methods, along with other research endeavors, have achieved an efficiency rate close to 100%. Wang et al. [78] conducted a comparative analysis between the performance of a bioaugmented microbial culture immobilized in the MBBR and that of a suspended culture. In their study, they adapted aerobic granular sludge (AGS) in an SBR to treat petroleum wastewater. The modification involved the artificial introduction of heterotrophic nitrification–aerobic denitrification (HN-AD) bacterial strains into the microbial culture. The researchers conducted a comprehensive assessment of the bioaugmented sludge's effectiveness by comparing its treatment performance with that of suspended and unmodified culture in 1.8 L bioreactors. The bioreactors operated in alternating anaerobic–aerobic modes at room temperature. The individual strain tests focused on nitrogen removal from synthetic wastewater, revealing that Pseudomonas mendocina K0, *Brucella* sp. K1, *Pseudomonas putida* T4, and *Paracoccus* sp. T9 were the most efficient bacteria for incorporation into the AGS. These strains demonstrated superior capabilities in treating both ammonia and nitrate nitrogen. Upon introducing these selected strains into an AGS within a Sequencing Batch Reactor (SBR) and acclimating them to synthetic petroleum influent, the microbial community exhibited a remarkable $\%RE_{TN}$ and $\%RE_{NH4}$ of 80% and 92%, respectively. This performance significantly surpassed that of the control bioreactor lacking the bioaugmented culture, which achieved a $\%RE_{TN}$ and $\%RE_{NH4}$ of only 26% and 83%, respectively. Furthermore, this deliberate manipulation of species diversity resulted in a 17% increase in settleable AGS granule formation and a striking 400% higher abundance of nitrate reductase.

Bioreactors utilizing biofilms are reliant on process parameters akin to those found in suspended tanks, encompassing factors such as temperature, pH, HRT, and substrate concentration in the medium. Yet, a distinctive and progressively investigated factor for improving nitrogen treatment through immobilized cultures is the choice of biocarrier material. This material selection plays a crucial role in regulating various aspects, including surface area for growth and any potential pores or internal structures that promote microbial growth. Jiang et al. [79] conducted an experiment utilizing polyvinyl alcohol/sodium alginate (PV/SA) beads layered double hydroxides (LDHs) to immobilize bacteria used to remove ammonia, nitrate, nitrite, and TN from synthetic wastewater through nitrification–denitrification. The 200 mL immobilized bioreactor, filled to 10% of its volume, operated at 26 °C and a pH of 8, showed excellent treatment efficiency. The addition of 0.6 g MgAl-LDHs allowed for the removal of 90%, 90%, and 98% of $\%RE_{NH4}$, $\%RE_{NO3}$, and $\%RE_{NO2}$. Interestingly, other biocomposites made with higher LDH additives (0.8 and 1.2 g) showed weaker treatment efficiencies and longer acclimation times. *Acinetobacter*, *Delftia*, *Stenotrophomonas*, and unclassified genera of the *Enterobacteriaceae* and *Rhizobiaceae* families were most dominant and responsible for the nitrification–denitrification process. Pang et al. [80] showed how the anammox treatment could improve nitrogen removals from various raw materials processed by the addition of biochars as biocarriers. The 500 mL anammox reactor, operated as an SBR at 35 °C, pH = 7, and HRT = 48 h, achieved a $\%RE_{TN}$ and $\%RE_{NH4}$ and a NO_2^--N removal efficiency of 85%, 90%, and 95%, respectively. The obtained performance not only exceeded the control culture without biocarriers, but was also better than that with other biocarriers such as quartz sand and polyethylene. It was highlighted that the high removal rates of ammonia and nitrite were due to the presence of an abundance of anammox bacteria. Nguyen et al. [81] enhanced the SND process by coating clay biocarriers with alginate and essential nutrients. In such configurations, the 15 mL batch reactors, operated for 24 h at room temperatures and with a pH in the range of 7–8, showed $\%RE_{TN}$, $\%RE_{NH4}$, and $\%RE_{NO2}$ treatment efficiencies of 92%, 84%, and 99%, respectively. The microbial community was selectively chosen to contain *Nitrosomonas* sp., *Nitrobacter* sp., and *Bacillus* sp. While these results show promise, it is essential to note that the bioreactors used were insufficiently sized to extrapolate the efficacy of this method on a larger scale. Due to the limited working volume, several ideal assumptions, such as uniform conditions in temperature, pH, and microbial community, were applicable. Additionally, each bioreactor accommodated only one granule of bacteria-covered clay, further simplifying the complexities associated with operating a wastewater treatment system. Ni et al. [82] utilized basalt fiber (BF) biocarriers for the immobilization of a microbial culture to treat nitrogen content in highly resilient lithium battery slurry wastewater. It was suggested that the BF offers a large surface area, corrosion resistance, and the ability to form a three-dimensional structure that allows for both anoxic and oxic layers to form for SND. The 3.6 m^3 R-BF reactor, which contained 360 bundles of BF biocarriers and operated at HRT = 12 h, 27 °C, and pH = 7.6, was compared with an activated sludge reactor operated under similar conditions. The BF bioreactor showed superior TN and NH_4^+-N removal efficiencies of 77% and 75%, respectively, compared to 62% and 65% for the activated sludge bioreactor. Furthermore, calculations showed that the total nitrogen removal rate and substrate maximum specific reaction rate were 4.462 $kg/m^3/d$ and 0.323 mg N/mgVSS/d, respectively. Microbial analysis revealed a dominance of denitrifying *Ottowia* and *Chujaibacter* and heterotrophic nitrifying *Hydrogenophaga* and *Thauera*. Zhu et al. [83] utilized polyurethane sponges for a partial nitrification and annamox (PNA) treatment in an SBR to treat ammonia from municipal wastewater. The 10 L SBR, filled to 20% of its total volume with polyurethane sponge biocarriers and operated in an anaerobic (HRT = 1.5)–aerobic (HRT = 5.5)–anoxic (HRT = 2) manner at 25 °C showed a $\%RE_{TIN}$ and $\%RE_{NH4}$ of 93% and 97%, respectively. It was highlighted that the dissolved oxygen in the three stages to achieve this high removal should be 0.05, <1, and 0.05 mg/L, respectively. The most dominant bacterial genera were generally *Candidatus Brocadia*, *Nitrospira*, *Candidatus Competibacter*, *Candidatus Accumulibacter*, *Rhodoplanes*, *Denitratisoma*, and *Thauera*, although *Nitrosomonas* was also detected to a lesser extent, exhibiting a wide variety in anammox, ammonia-oxidizing, nitrite-oxidizing, and denitrifying bacteria. Hybrid biocarriers can be synthesized for optimal nitrogen performance. Zou et al. [84] developed hybrid biocarriers consisting of calcium carbonate, powdered activated carbon, and polyvinyl alcohol. The developed biocarriers were designed to resist the sheer produced in Chinese metal mining wastewater. The 650 L bioreactor, filled to only 8% and operated at 28 °C under a nitrification–denitrification mode with an HRT in each chamber of 3.4 h and a pH = 7.8 achieved TN and NH_4^+-N removal rates of 0.51 $kg.m^{-3}.d^{-1}$ and 0.43 $kg.m^{-3}.d^{-1}$, respectively, with corresponding average removal efficiencies of 97%. Microbial community analysis of the fillers showed the nitrification community to be dominated by *Nitrosomonas*, *Nitrospira*, *Aridibacter*, and *Prosthecobacter*, while the denitrification biofilms were abundant in the genera *Thauera*, *Ottowia*, *Aquamicrobium*, and *Fusibacter* at the optimal performance period.

Other methods have been reported to enhance the treatment efficiency of MBBRs for nitrogen-rich wastewaters. Zheng et al. [85] propose using an air-lift reflux technique for the aeration of the bioreactor to reduce costs and sludge production in treating rural sewage. The reactor consists of anoxic and oxic sections with volumes of 0.125 and 0.375 m^3, corresponding to HRTs of 6 and 18 h, respectively. The temperature and pH were maintained at 26 °C and 7, respectively. Such a configuration achieved noticeable removal rates of $\%RE_{TN}$ and $\%RE_{NH4}$ up to 81% and 95%, respectively, compared with 67% and 74% in the non-reflux bioreactor. The results confirm the benefits of the aeration method in enhancing the process efficiency and reducing sludge production by 42%. Nevertheless, as the authors performed the no-reflux cultivation immediately after inoculum extraction, the microbial community may not be as acclimated compared to the reflux experiments. This raises questions about the observed difference between the two modes. The most dominant bacteria were *Nitrospira*, *Nitrosomonas*, *Denitratisoma*, and *Thauera*.

Regulating the dissolved oxygen levels in the cultivation medium presents a straightforward means of influencing the activity of specific species and, consequently, the nitrogen removal pathway. In a study by Bian et al. [86], the impact of dissolved oxygen on nitrogen removal efficiency was investigated in a Submerged Aerobic Fixed Film Moving Bed Biofilm Reactor (SND MBBR) treating synthetic wastewater with a high C/N ratio. Biocarriers, in the form of pall rings, filling 40% of the 5 L reactors, were employed under various DO concentrations (0.5, 1.5, and 3.5 mg/L), at 25 °C and HRT = 24 h. Results revealed that at a DO concentration of 1.5 mg/L, the maximum $\%RE_{TN}$ and $\%RE_{NH4}$ were 85% and 100%, respectively. These values were significantly higher compared to those achieved at 0.5 mg/L (65% and 80%). Lower doses of DO not only lead to reduced $\%RE_{NH4}$ but also saw its reappearance as NO_2^--N in the effluent, resulting in diminished TN treatment efficiencies. While the performance at 3.5 mg/L DO surpassed that at 0.5 mg/L, it still fell below the mid-point. This can be attributed to an elevated rate of metabolic electron generation and transfer to the denitrification process. The most abundant genera detected in the mixed culture were *Acinetobacter*, *Paracoccus*, *Nitrosomonas*, and *Thauera*, with the dominant nitrogen removal pathway being partial SND.

Shao et al. [87] investigated the removal rates of TN in an anaerobic biofilm reactor (ABR) after a cultivation period for a full-scale tofu processing system. The 24 m^3 ABR operated at an HRT = 23H, 48 °C and pH = 7.5. It is reported that after the 50th day of cultivation, the bioreactor showed a superior performance, with an average $\%RE_{TN}$ and $\%RE_{NO3}$ of 78% and 86%, respectively.

Nevertheless, a distinct reduction in treatment effectiveness was observed subsequently, coinciding with a rise in the concentrations of NH_4^+-N and NO_2^--N in the effluent, while the nitrate nitrogen removal rate remained steady. The analysis of the microbial community showed the presence of *Rhizobium*, *Flavihumibacter*, *Caldilineaceae*, and *Desulfomicrobium*. The trend of denitrification reduction coincided with the death of microbial species containing nitrite reductase and nitric oxide reductase enzymes. This occurred due to the high COD/N ratio of 7.3–9.1 in the initial stages, proven by the return of high removal rates when this ratio was decreased.

Biofiltration is another example of immobilized growth-based bioreactors. Microbial culture grows on filter material, leading to the existence of a biological layer that treats wastewater by both biological uptake, filtration, and even adsorption. Ren et al. [88] investigated the combined effect of microbial growth and an adsorption process consisting of an iron-loaded biological activated carbon filter (Fe-BACF). The design involves a small 0.5 L tubular reactor housing the BACF and operated at 10 °C. The filtration rate, backwashing intensity, and period were set at 0.3 m/h, 1.5 L/m^2.s, and 2 weeks, respectively. Analysis of the influent and effluent showed a decrease in NH_4^+-N concentration from 5–6 mg/L to around 0.1 mg/L, corresponding to a 98% removal efficiency compared to the 88% achieved without the addition of Fe. Unfortunately, due to the nature of the reactor, only nitrification occurred as the NO_2^--N and NO_3^--N levels in the effluent were around 1 and 4 mg/L, respectively. Microbial community analysis showed that the addition of iron to the filter increased the compositions of *Nitrosomonas* and *Nitrospira* significantly, but not *Azoarcus*, *Comamonas*, and *Methyloversatilis*. Though total nitrogen content in the wastewater was not efficiently removed, the enhanced biofilter showed promising ammonia nitrogen removal efficiencies in cold temperatures and low nitrogen concentrations, which was made possible by enhanced surface area, pore volume, and microbial activity. Aguilar et al. [89] reported the effect of aeration on the performance of an artificial mobile wetland containing a cork-based filling/filter for microbial immobilization. The authors had previously reported the operational feasibility of such a biosystem in a previous study. The 39 m^3 aerated vertical-flow wetland had a 14 m^2 surface area and a 1.4 m deep cork filter/filling and operated at an HRT of 13 days for 5 months each under an aeration or non-aeration mode. Effluent analysis revealed the aerobic mode to be superior in terms of $\%RE_{TN}$ and $\%RE_{NO3}$ treatment, with removal efficiencies recorded at 83% and 95%, respectively, compared to the 37% and 42% achieved in the anaerobic mode, interestingly implying that aerobic denitrifying bacteria exist in higher abundance than traditional ones. Although microbial species analysis was not conducted, qPCR analysis revealed the aerobic mode to contain higher numbers of the *nosZ* and *nirS* enzymes, both responsible for the denitrification pathway.

Biological treatment systems have a well-established history with filtration technology, and there is a growing interest among researchers in using membrane technology for nitrogen removal. In the study by Liu et al. [90], membrane technology was integrated with the conventional aerated attached growth method to address low COD/N wastewater, which characterizes landfill leachate. The two-stage bioreactor is composed of an inner cylindrical chamber containing the membrane biofilm and an outer cylindrical chamber containing the packing material in which aeration is supplied. The 30 L system, which was operated at an HRT = 24 h and COD/N ratio in the range of 2.3–1.5 exhibited a $\%RE_{TN}$ and $\%RE_{NH4}$ of 86% and 90%, respectively. Meanwhile, nitrification and denitrification rates/contributions to the $\%RE_{TN}$ and $\%RE_{NH4}$ were 71% and 51%, indicating that the removal mechanism is through the SND thanks to the *Proteobacteria*, *Bacteroidota*, and *Patescibacteria* phylum microbial community. Varying the COD/N ratio above and below 2.3–1.5 resulted in a sharp decrease in efficiency. Inaba et al. [91] investigated the feasibility of treating nitrogen-rich wastewater from the ironworks industry utilizing an aerated anaerobic membrane bioreactor supplied with methanol as a carbon source. The bench (0.026 m^3) and pilot scale reactors (4 m^3), having influent flow rates of 0.0022 and 0.69 m^3/day and operated at 23 and 30 °C and pH levels around 8.4, respectively achieved complete (~100%) NO_3^--N removal efficiency after 50 days of cultivation. Before that, the microbial community underwent acclimation and achieved a removal rate of 1.1 kg NO_3^-N/m^3/day, which was deemed competitive with values reported in the literature. The utilization of nitrogen gas for agitation purposes was a necessary and cost-effective replacement for air/oxygen to maintain anaerobic conditions. In addition, the proposed method requires a steady supply of the methanol, which might decrease its attractiveness for large-scale applications. The bacterial species *Hyphomicrobium nitrativorans* showed the highest abundance (25–68%) in this system, suggesting the dominance of denitrifying strains amongst the mixed culture. This technology is subject to optimization, mostly in the form of membrane material selection. Zhang et al. [92] replaced traditional activated carbon material (GAC) with sponge iron (SI) that would supply iron ions to enhance electron transfer in an SND membrane bioreactor; this action was observed to enhance the treatment of nitrogen wastewater. This was confirmed by conducting bacterial cultivation in a GAC-MBR and an SI-MBR in 20 L and 4 L bioreactors. The reactors, which were operated at an HRT = 12 h, 25 °C, and pH = 7.3, had dedicated anoxic sections. After 60 days of cultivation, a COD removal efficiency of 93% was achieved by the SI-MBR, compared to 87% in the GAC-MBR. The ammonia nitrogen removal efficiency was remarkably similar for both bioreactors, reaching up to 99% with a slight negligible advantage towards activated carbon. Additionally, the SI-MBR achieved excellent nitrification and denitrification rates of 3.5 and 6.6 mg/g VSS.h, respectively. The analysis of microbial communities showed a high abundance of the genera *Nitrospira*, *Pseudomonas*, and *Thermomonas*, while some others that were increased due to sponge iron were *Thiobacillus* and *Sideroxydans*.

A more novel technology of nitrogen removal was investigated by Cao & Fan [93], who attempted to treat synthetic wastewater by the reported natural ammonia oxidation to nitrogen gas in a microbial electrochemical cell. The 1 L cell, which was operated at 25 °C and a pH of 7.5, showed up to 95% of NH_4^+-N removal at an applied potential of 0.3 V. The dominant microbial species were *Nitrospira* sp. and *Bryobacter* sp. However, the TN removal efficiency was 88%, indicating that some of the ammonia nitrogen was converted to nitrate/nitrite and could not be converted to N2 by the existing anaerobic community.

Table 4. Immobilized growth bioreactors for treating nitrogen-rich wastewaters.

Immobilization Medium	Bioreactor	Influent Conc.	Removal Efficiency	Dominant Bacteria	Reference
Polyethylene	V: 4 m^3 HRT: 139 h T: 30 °C pH: 8.4	NO_3^--N: 6650 mg/L	NO_3^--N: 100%	*Hyphomicrobium nitrativorans*	[91]
Polyvinyl Alcohol/Sodium Alginate	V: 200 mL T: 26 °C pH: 8.0	TN: 40 mg/L NH_4^+-N: 20 mg/L NO_3^--N: 10 mg/L NO_2^--N: 10 mg/L	TN: 93% NH_4^+-N: 90% NO_3^--N: 90% NO_2^--N: 98%	*Acinetobacter* *Stenetrophomonas*	[79]
Polyethylene	V: 4935 m^3 HRT: 9.8 h T: 20 °C pH: 7.5	TN: 72 mg/L NH_4^+-N: 60 mg/L	TN: 74% NH_4^+-N: 99%	*Methylotenera* *Nitrosomonas* *Nitrospira*	[77]
Carbon Felt	V: 1 L T: 25 °C pH: 7.5	NH_4^+-N: 50 mg/L	NH_4^+-N: 95%	*Nitrospira* sp. *Bryobacter* sp.	[93]
Volcanic Rocks	V: 0.5 m^3 HRT: 24 h T: 26 °C pH: 7	TN: 53 mg/L NH_4^+-N: 34 mg/L	TN: 81% NH_4^+-N: 95%	*Nitrospira* *Nitrosomonas* *Denitratisoma* *Thauera*	[85]
N.A *	V: 5.6 m^3 HRT: 11.2 h T: 27 °C pH: 7	TN: 53 mg/L NH_4^+-N: 52 mg/L	TN: 92% NH_4^+-N: 98%	*Nitrospira* *Nitrosomonas* *Thauera* *Dechloromonas*	[76]

Table 4. *Cont.*

Immobilization Medium	Bioreactor	Influent Conc.	Removal Efficiency	Dominant Bacteria	Reference
Iron-loaded Activated Carbon	V: 0.5 L T: 10 °C	NH_4^+-N: 6 mg/L	NH_4^+-N: 98%	*Azoarcus* *Comamonas* *Methyloversatilis*	[88]
Coal Biochar	V: 500 mL HRT: 48 h T: 35 °C pH: 7	TN: 205 mg/L NH_4^+-N: 100 mg/L NO_2^--N: 105 mg/L	TN: 85% NH_4^+-N: 90% NO_2^--N: 95%	*Candidatus Jettenia* *Candidatus Brocadia*	[80]
Alginate-coated Clay	V: 15 mL HRT: 24 h T: 25 °C pH: 7.5	TN: 60 mg/L NH_4^+-N: 30 mg/L NO_2^--N: 30 mg/L	TN: 92% NH_4^+-N: 84% NO_2^--N: 99%	*Nitrosomonas* sp. *Nitrobacter* sp. *Bacillus* sp.	[81]
N.A	V: 5 L HRT: 24 h T: 25 °C	TN: 100 mg/L NH_4^+-N: 100 mg/L	TN: 85% NH_4^+-N: 99%	*Acinetobacter* *Paracoccus* *Nitrosomonas*	[86]
Sponge Iron–Polyvinylidene Fluoride	V: 20 L HRT: 12 h T: 25 °C pH: 7.3	NH_4^+-N: 27 mg/L	NH_4^+-N: 99%	*Nitrospira* *Pseudomonas* *Thermomonas*	[92]
N.A	V: 30 L HRT: 24 h	TN: 189 mg/L NH_4^+-N: 46 mg/L	TN: 86% NH_4^+-N: 90%	*Proteobacteria* *Bacteroidota*	[90]
N.A	V: 24 m^3 HRT: 23 h T: 48 °C pH: 7.5	TN: 62 mg/L NO_3^--N: 59 mg/L	TN: 78% NO_3^--N: 86%	*Rhizobium* *Flavihumibacter* *Caldilineaceae* *Desulfomicrobium*	[87]
Polyvinyl Alcohol–Powdered AC–Calcium Carbonate Hybrid	V: 1300 L HRT: 3.4 h T: 28 °C pH: 7.8	TN: 136 mg/L NH_4^+-N: 101 mg/L	TN: 97% NH_4^+-N: 97%	*Nitrosomonas* *Thauera* *Ottowia*	[84]
Basalt Fiber	V: 3.6 m^3 HRT: 12 h T: 28 °C pH: 7.6	TN: 238 mg/L NH_4^+-N: 170 mg/L	TN: 77% NH_4^+-N: 75%	*Ottowia* *Chujaibacter* *Thauera* *Hydrogenophaga*	[82]
Polyurethane Sponge	V: 10 L HRT: 18 h T: 25 °C	NH_4^+-N: 67 mg/L	TN: 93% NH_4^+-N: 97%	*Candidatus Brocadia* *Nitrospira* *Denitratisoma* *Thauera*	[83]
Biochar	V: 1.8 L T: 25 °C	TN: 65 mg/L NH_4^+-N: 65 mg/L	TN: 80% NH_4^+-N: 92%	*Pseudomonas mendocina* *Brucella* sp. *Pseudomonas putida* *Paracoccus* sp.	[78]
Cork Granules	V: 39 m^3 HRT: 13 d pH: 7.7	TN: 24.2 mg/L NO_3^--N: 15.7 mg/L	TN: 83% NO_3^--N: 95%		[89]

* Not available/mentioned.

The immobilized growth system offers numerous advantages as an effective method for nitrogen removal from wastewater. These benefits include decreased mortality rates, a clear separation between biological sludge and the liquid phase, improved treatment efficiencies, and the development of strong biological structures that support both aerobic and anaerobic growth. This technique also offers the benefit of bioaugmentation, which enhances the efficiency of ammonia and nitrate removal in microbial cultures. Different biocarrier materials are essential for controlling the growth of microorganisms in bioreactors. An illustration of the application of polyvinyl alcohol/sodium alginate beads layered double hydroxides (PV/SA LDHs) is the immobilization of bacteria for the purpose of ammonia removal, resulting in a remarkable treatment efficiency. The hybrid biocarriers exhibited a high percentage of removal for both $\%RE_{TN}$ and $\%RE_{NH4}$. Integrating air-lift reflux techniques into bioreactor designs resulted in a substantial enhancement of $\%RE_{TN}$ and $\%RE_{NH4}$, along with a reduction in sludge generation. The use of an immobilized growth system can also increase the amounts of dissolved oxygen and raise the effectiveness of nitrogen removal. The combination of membrane technology and standard aerated attached growth methods is being explored to highlight the potential of membrane bioreactors in treating low COD/N effluent. The results collectively illustrate the adaptability and efficiency of immobilized growth systems in different bioreactor setups for removing nitrogen from several types of wastewater. The selection of the biocarrier material, process parameters, and system design is essential for attaining optimal performance and treatment efficiency.

4. Physico-Chemical Removal of Nitrogen

4.1. Air Stripping

This process is a firmly established desorption method wherein ammonia (NH_3) is eliminated from wastewater using either air or steam. The underlying chemical principle involves the dissolution of ammonia gas, a weak base in water, acting as a weak acid. This results in the formation of the ammonium ion and a hydroxide, reducing the water body's pH (See Reaction (5)).

$$NH_{3(g)} + H_2O_{(L)} \rightarrow NH_4{}^{+}{}_{(aq)} + OH^{-}{}_{(aq)} \quad (5)$$

By adding alkalinity (e.g., $CaCO_3$) and increasing the pH of this system, the reaction can be forced to the left, completely converting all ammonium to ammonia. The introduction of such a treated system could then be introduced to a stripping column, where ammonia is to be removed at the top. This is corroborated through practical observations [94], where the rate of ammonia removal was found to be most significantly influenced by pH (with an optimal value of 10.5). Subsequently, the aeration rate exhibited a positive correlation, while the presence of zinc in the water intensified this dependency. This enhancement was attributed to the formation of zinc oxide, which absorbed ammonia. The effects of pH, aeration rate and even temperature have been further proven in other research [36,95,96], with the ideal conditions considered to be around a pH of 11, aeration rate of 4–6 L/min, and a typical column height of up 7.6 m. The temperature is an important parameter, which positively correlates with ammonia removal efficiency ($\%RE_{NH4}$) [97]. Increasing the temperature increases the dissociation constant of $NH_4{}^+$ and decreases the solubility of the free ammonia gas in the water. The effect of all the mentioned parameters was studied in the treatment of municipal wastewater from the city of Ahvaz, Iran [31]. It was observed that increasing the pH from 11 to 12.5 led to an increase in $\%RE_{NH4}$ from 70% to almost 100% when other parameters were fixed. Upon examining the temperature variations, it was found that the $\%RE_{NH4}$ was merely 6.6% at 34 °C but increased to 98% at 45.8 °C. Notably, under the highest tested air-to-water ratio of 80, the removal efficiency reached its peak within the range of 56% to 98%.

Unfortunately, the traditional approach to ammonia air stripping possesses numerous drawbacks [98], with one of the notable issues being its comparatively elevated expense, particularly when contrasted with the biological alternative. The cost could be reduced by microwave pretreatment of the liquid going in the stripper, as reported by Yin et al. [99]. The results showed that applying microwave pretreatment enhanced the mass transfer coefficient and stripping efficiency (up to 99.25%) at lower gas-to-liquid ratios. This occurs because the microwave heat increases the kinetic energy at the molecular level. This technology's cost could be further reduced by replacing the microwave treatment with high-frequency electric fields [100], which could induce a similar effect to microwaves [100].

It was reported that a frequency and strength of 50 MHz and 15 V/cm could increase the $\%RE_{NH4}$ up to 94.3%. The column could be improved as well, as is discussed in detail in other research regarding water-sparged aero cyclones [101].

The change of ammonia–ammonium as a function of pH plays a key role during the treatment process. The ionic compounds ammonium (NH_4^+) and hydroxide (OH^-) are formed when NH_3 (ammonia) is dissolved in water, as per Equation (5). The pH of the solution has a major impact on the location of this equilibrium, as is illustrated by Figure 3. When the pH of a solution is basic, more hydroxide ions (OH^-) are present and NH_4^+ is formed, tipping the equilibrium in favor of the right. Therefore, there is a greater abundance of ammonia in the form of NH_4^+ in alkaline settings. On the other hand, hydrogen ions (H^+) in an acidic solution shift the equilibrium to right, and NH_3 is formed, changing the equilibrium to the left. Therefore, there is more unionized ammonia present in acidic situations. The pKa of the NH_4^+/NH_3 system is defined as the pH at which 50% of the ammonia is in the ionized form (NH_4^+) and 50% is in the unionized form (NH_3). At room temperature, ammonia has a pKa of 9.25. Ammonia is present as ammonium ions below this pH and as unionized ammonia above this pH. Since the pH of a solution can have a major impact on ammonia's toxicity, mobility, and ability to be removed from wastewater, knowing how the ammonia–ammonium equilibrium relates to pH is crucial in many environmental and industrial settings.

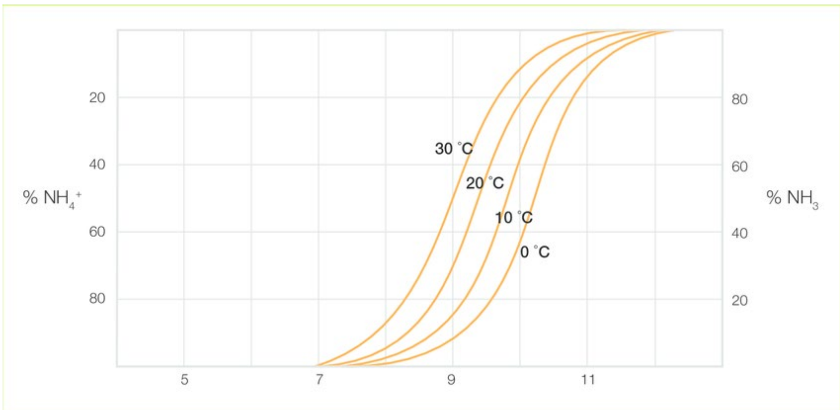

Figure 3. Ammonia–ammonium equilibrium location with pH [102].

4.2. Adsorption and Ion Exchange

Most commonly, activated carbon, also known as activated charcoal, is used for the adsorption of ammonia/ammonium nitrogen, with the most important process parameters being pH, adsorbent dosage, and contact time [103]. Ren et al. [104] investigated the removal of ammonia nitrogen from low temperature synthetic water using activated carbon as the adsorptive material, loaded with iron (Fe-AC). The $\%RE_{NH4}$ was 31% at an adsorbent dosage of 1.6 g, while the adsorption capacity at a pH = 7 was 0.15 mg/g. According to the authors, the addition of Fe to the AC was proven to enhance the removal rate and adsorption capacity. Additionally, applying organic acid on the AC adsorbent's surface enhances its performance for the removal of ammonia from landfill leachate [30]. The addition of the organic acid to the adsorbent enhanced its experimentally measured $\%RE_{NH4}$ from 64% to 94%, and the adsorbent capacity was increased from 1.48 to 3.06 mg/g.

Treatment of wastewater by zeolites, particularly natural zeolites, is a possible pathway for cost savings and good removal efficacy [105]. Kannan & Parameswaran [38] utilized the natural zeolite clinoptilolite for the treatment of TAN from swine wastewater permeate. The adsorbent was demonstrated to completely remove all TAN from real swine wastewater (108 mg/L TAN) inside the batch reactor in about 47 h, and 37 h for synthetic wastewater (400 mg/L TAN). The pseudo-first-order and pseudo-second-order adsorbent capacities of the zeolite were 14.41 and 15.8 mg/g when treating synthetic wastewater, respectively. The Thomas model-based calculated adsorbent capacity was 9.81 mg/g when treating real swine wastewater. The two authors also witnessed how different existing cations showed an inhibitive effect on the adsorbent/ion exchanger by competing with nitrogen on the capture sites, and potassium showed the highest inhibitive effect, decreasing the adsorption capacity by 60%. This inhibitive effect by competing cations has also been witnessed in other experimental data [106]. Other research uses natural zeolite (85% clinoptilolite) to remove ammonium, dissolved COD, and colors from sanitary landfill leachate [29]. The percentage removal of NH_4^+-N, dCOD, and color at a pH of 7, zeolite dosage of 133 g/L, particle size of 0.930 µm, and stirring rate 1.18 m/s for 2.5 min were ~52%, 51%, and 25%, respectively. The maximum adsorbent capacity was found to be 3.59 mg/g, according to the Langmuir model. The regeneration of the zeolite was demonstrated to increase the $\%RE_{NH4}$ by 40%. There is potential for this technology to be enhanced by further incorporating it with other materials. For example, rice straw, which has natural nitrogen removal properties, can be integrated with natural zeolite (Si/Al: 4.25–5.25) as an adsorbent for the treatment of wastewater [107]. The integrated zeolite/rice straw adsorbent showed a $\%RE_{NH4}$ and total nitrogen removal efficiency ($\%RE_{TN}$) of 49–78% and 40–66%, respectively, from synthetic wastewater simulating farmland runoff. This removal efficiency was 1.5–3 times higher than those obtained from the zeolite alone. Meanwhile, the $\%RE_{NO3}$ and $\%RE_{TN}$ from synthetic wastewater were 68–83% and 46–62%, respectively. Interestingly, the rice straws were also shown to be viable biocarriers for denitrifying bacteria, enhancing the removal even further by incorporating the biological removal of nitrogen into the adsorption process.

Although AC and zeolites are the most common adsorbents for wastewater treatment, more materials continue to appear as viable candidates [108]. The use of a bentonite adsorbent modified with aluminum and tannin for the treatment of low temperature domestic sewage wastewater (Al-Tan-Bent) was introduced by Cheng et al. [26]. More than 75% of NH_4^+-N was removed from wastewater under optimal conditions, and the adsorption capacity based on monolayer adsorption was calculated to be 5.85 mg/g. The addition of tannic acid enhanced the $\%RE_{NH4}$ from 35% to 75%. Other parameters shown to significantly affect the treatment process are pH, adsorbent dosage, and contact time. Other examples of alternative materials used as adsorbents include titanate-based adsorbent [109,110], ceramsite sand [32], and ceramic [17,106], among others.

Ion exchange could remove nitrogen from wastewater, specifically, nitrogen in the form of ions (e.g., NH_4^+, NO_2^-, NO_3^-) [111–113], although in principle, ion exchange is different from adsorption, as adsorption is the removal of molecules from a fluid and their attachment to the surface of an adsorbent material. Ion exchange is specifically the removal of ions from the solution by resins that selectively replace ions in the solution with ions in the ion exchanger medium. The boundary separating these two processes can be blurry when removing previously mentioned nitrogen-containing compounds. For this reason, the two terms are sometimes used interchangeably, and their performance parameters and indicators are similar (e.g., contaminant removal capacity, mg/g). Alshameri et al. [114] investigated the ion exchange capability of Yemeni natural zeolite (NZ) on the removal of the ammonium ion from synthetic wastewater, along with a sodium-modified version of the zeolite (SNZ). The NZ was mostly made of 69.9% silicon and 11.8% aluminum oxides, while the SNZ had higher silicon dioxide and Na_2O fractions and lower CaO and K_2O fractions. Both were used to treat wastewater containing 80 mg/L NH_4^+ at 25 °C and a pH of 7. SNZ exhibited a $\%RE_{NH4}$ exceeding 92% within just 20 min in the batch system, in contrast to NZ, which achieved a $\%RE_{NH4}$ slightly over 80% after a 120 min operation. This variation in performance can be attributed to the lower CaO and K_2O values in SNZ, as calcium and potassium ions act as robust competitors at the ion exchange site. The efficiency of NH4+ removal increases with a pH up to 7/8, but subsequently decreases due to ammonia formation. Moreover, higher initial ammonium concentrations adversely affect removal rates. Under equilibrium conditions at 35 °C and a pH of 8, SNZ demonstrated a maximum $\%RE_{NH4}$ and capacity of 99% and 11.8 mg/g, respectively. More recent research sheds light on the life cycle assessment of ion exchange for the removal of ammonium nitrogen from municipal wastewater using synthetic zeolite ($K_{12}Al_{10}Si_{10}O_{40}Cl_28H_2O$) [33]. With the variance in influent ammonium nitrogen concentration that is common in municipal wastewater, the ion exchange capacity and $\%RE_{NH4}$ varied between 0.9–17.1 mg/g and 28–96%, respectively. At exceptionally low concentrations of NH_4^+-N (<2.5 mg/L), the zeolite was found to release up to 12% of the NH_4^+-N into the wastewater. This problem was avoided at medium initial concentrations, and the removal efficiency peaked at higher values. Regeneration by brine (KCl) gave a regeneration efficiency of 94% at the first cycle, which decreased to ~25% with cycles 2–6. The decrease in efficiency after the second regeneration was attributed to the increase in the mass of the ammonium in the ion exchange medium. LCA concluded that the use of ion exchange technology followed by regeneration led to a reduction in cumulative energy demand, global warming potential, and marine eutrophication potential of 25%, 66%, and 62%, respectively. Additionally, this treatment process is feasible for the removal of nitrite and nitrate ions as well [115,116]. The $\%RE_{NO2}$ and $\%RE_{NO3}$ were reported to be at least 71% and >95% when ion exchange was coupled with electrodes to treat dyeing wastewater. The optimum conditions were determined using response surface methodology.

4.3. Membrane

Membrane distillation is a physico-chemical separation process that is very similar in principle to air stripping. This process is based on the equilibrium between ammonia and the ammonium ion. It is dependent on pH levels: a higher pH leads the reaction (Equation (5)) to shift to the left, producing ammonia in the gaseous phase, which is then separated from the wastewater by the flow of the ammonia through a selective membrane. Intrchom et al. [117] investigated the efficacy of the removal of ammonia in carbon nanotubes (CNTs) immobilized in membranes as opposed to the more traditional polytetrafluoroethylene (PTFE) membranes. The CNTs showed superior performance compared with PTFE, and polar carboxylated CNTs (f-CNTs) had even better performance than raw CNTs. A solution with an initial concentration of 300 mg/L showed a $\%RE_{NH4}$ of 14% at 40 °C by f-CNTs. The flux rate was 63% and 22% higher than those obtained from PTFE and raw CNTs, respectively. The superior performance of f-CNTs was attributed to the carboxylic functional groups, which enhance ammonia sorption. Zico et al. [28] propose a membrane distillation design that incorporates solar energy to recover ammonia from landfill leachate. The addition of sulfuric acid enhanced the capture of ammonia by converting it to ammonium sulfate. Optimum conditions (pH: 10.8, T: 43 °C, H_2SO_4: 0.18 M) were used for $\%RE_{NH4}$ and recovery rates of 98% and 59%, respectively. Supplying solar energy instead of electricity to the membrane reduced the operating cost for the process by about 16%. To shed light on the feasibility of using membrane technology to treat biogas slurry without pH adjustments, Shi et al. [118] conducted a techno-economic analysis of vacuum membrane distillation that concluded that the process is economically feasible. With an ammonia separation factor that can go up to 8.05, the net profit decreased when applying sodium hydroxide for increasing pH levels, and it increased significantly with the increase in influent TAN content.

The utilization of membrane-aerated biofilm reactor (MABR) technology for wastewater treatment is well established [119]. Microorganisms in biofilm are immobilized on the surface of the membrane, and the air/oxygen diffuses through the membrane walls to supply O_2. Many crucial factors, such as contaminant loading rates, pH levels, and hydraulic retention time (HRT) should be considered during optimization. Mei et al. [18] employed an MABR to remove nitroaniline (NA) from synthetic wastewater while simulating a dye factory. The membrane tubes were made of silicon rubber, and they are supported by epoxy resin. The microbial community in the biofilms was dominated by *Proteobacteria* and *Bacteroidetes*. At the optimum conditions, the removal loading rate and $\%RE_{NH4}$ were 0.118 kg/m^3.d and 98%, respectively, while the $\%RE_{TN}$ and $\%RE_{COD}$ were 88.52% and 82.40%, respectively. The authors affirm the technology's prospects for industrial use for the simultaneous removal of TN and NA. In addition to the biofilm on the membrane surface, one could also incorporate biocarriers for higher biomass yield, as in the study by Siriweera et al. [27], who demonstrated the treatment of domestic wastewater by MABR with polyvinyl alcohol biocarriers to immobilize denitrifying bacteria. In the existence of PVA gel, all the performance parameters increase with an increasing HRT. At an HRT of 12 h, the efficiencies of $\%RE_{COD}$ and $\%RE_{TN}$ and nitrification were 95.1% and 79.1% and 88.3%, respectively. At the same HRT, the use of the PVA gel increased the maximum $\%RE_{NH4}$ and $\%RE_{TN}$ by 11% and 18%, respectively. When speaking of nitrogen-rich wastewater, urine wastewater is one example that comes to mind [120]. MABRs could be used for the treatment of high strength wastewaters [35]. Depending on the type of wastewater source (space stations: EPB vs. ISS vs. urine vs. humidity condensate), the organic nitrogen and carbon removal rates varied between 30–81% and 80–99%, respectively. At a high pH (>8), the removal rate of organic nitrogen is inhibited by the evolution of free ammonia. The microbial community was observed to be dominated by *Nitrosomonas*, *Nitrosospira*, *Nitrobacter*, and *Nitrosococcus*. The authors confirm that the use of MABRs in these scenarios has advantages such as little maintenance required and low-volume capability. In their research regarding the feasibility of an MABR for the treatment of urine wastewater simulating space habitation wastewater in a silicon-based membrane reactor [41], Landes et al. explain that the low efficiencies from this technology are due to the high nitrogen content along with low values of the organic carbon-to-nitrogen ratio, meaning less growth of microorganisms. Nevertheless, the nitrification and denitrification rates were recorded at 65% and 35%, respectively, while the $\%RE_{TN}$ and $\%RE_{NH4}$ removal rates were 36.5% and 61–70%, respectively. The authors maintain that this technology still has a future in such applications with low volumes of wastewaters [121].

Filtration is one of the oldest water treatment techniques known to humans. Thanks to advances made in technology, this process is tuned for even smaller particles, as in the case of ultrafiltration (UF) and nanofiltration (NF). This technology operates on the same principle as filtration, which is the flow of wastewater through a filter that captures very small pollutants (0.01–0.1 μm and 1–10 nm, respectively) to allow cleaner effluent to move out of the reactor [122,123]. Similar problems encountered in traditional filtration are also found in these more intensive filters, such as backwash requirements, fouling, and head loss, among others [124]. Cha et al. [34] propose the multilayer combination of a ceramic NF membrane with graphene oxide (GO) and polyethyleneimine (PEI) to treat semiconductor wastewater containing NH_4^+. With an increase in the number of GO/PEI bilayers, the water permeability decreased, and the ammonium retention (R_n) increased by about 8-fold when compared to that of pristine ceramic (no bilayers), and when tested against real semiconductor wastewater, it was shown that 3 bilayers had better ammonium retention than 10. The authors also evaluate the fouling resistance of this setup by determining the flux recovery ratios, and the bilayer addition of GO and PEI increased the FRR up to 71% and 91% for the three and ten bilayers, respectively (from 39%). Although this demonstrates potential, it does not necessarily mean filtration on its own could compete with other physico-chemical technologies. Luckily, the previously mentioned process could be coupled with more robust ones, such as biological treatment, as is shown in Qi et al.'s work, in which UF is combined with a membrane bioreactor and reverse osmosis [40]. While it was concluded after a nutrient fate analysis that UF on its own had a low recovery rate of 6.07% TN, and most of the nitrogen was removed by nitrifying and denitrifying bacteria, it still shows an increase in performance, and the overall thought is that this increase may or may not justify the extra costs associated with the installment and maintenance of the filters. Interestingly enough, the same paper also illustrates the possibility of using reverse osmosis (RO), a process commonly used for water desalination [125–127]. In RO, pressure above osmotic pressure is applied to control the flow of the water from the more contaminated section to the one with fewer solutes. In the previously mentioned study [40], the RO concentrate recovered up to 32% TN (and 21.4% P), which was higher than the UF, and the overall process that combined MBR, UF, and RO had a $\%RE_{TN}$ of 94.61%. Additionally, RO was used to recover ammonium nitrate (NH_4NO_3) from condensate water with a rejection rate of up to 90% of NH_4NO_3 at optimal conditions [128]. The optimum pressure of the RO filtration membrane was found to be reliant on pollutant content (concentrated vs. dilute), while other important parameters include temperature, pH, and initial influent concentration. A comprehensive operating expenses (OpExs) analysis was conducted to investigate the economics of membrane technologies [129] for wastewater treatment regarding COD removal, and multiple other researchers briefly mention preliminary results for economic analyses of membrane technology for nitrogen removal against conventional techniques [130,131], but there seems to be a gap in the literature concerning detailed techno-economic analyses of membrane technology for nitrogen removal from wastewaters.

5. Chemical Treatment

Chemical treatment of nitrogen-containing compounds in wastewater is possible in many ways, the most promising of which might be the advanced oxidation processes (AOPs). The AOPs are a set of chemical treatment processes that rely on the creation of a hydroxyl radical ($HO^{\bullet}$), a strong oxidant capable of oxidizing all compounds in wastewater. The AOPs attack the target contaminants, which are usually complex and non-biodegradable organic compounds, breaking them into smaller components that are easy to treat. The utilization of advanced oxidation processes (AOPs) in wastewater treatment, along with its compatibility with other conventional processes, has been previously investigated, revealing promising results [132–134]. Hydroxyl radicals can be generated by combining H_2O_2 with iron ions in what is known as Fenton's reagent (Equations (6)–(8)), through ozonation (Equations (9)–(12)) or UV light (Equation (13)). According to Zhou et al. [135], the highly toxic arsenic- and nitrogen-containing compound Roxarsone/ROX ($C_6AsNH_6O_6$) can be efficiently degraded by AOPs. A solar Fenton reaction was used to produce radicals by reacting Fe^{2+} with H_2O_2 in the presence of resorcinol formaldehyde resins to produce radicals. The $\%RE_{TOC}$ and rate of removal of emerging organic contaminants (EOCs) using this combination reached 75% and 50–64%, respectively; in addition, almost all arsenic was removed efficiently.

Advanced oxidation processes (AOPs) have emerged as effective techniques for removing organic nitrogen compounds from wastewater. Organic nitrogen compounds, often present in industrial and municipal wastewaters, include a variety of contaminants such as amines, amides, pyridine, and other nitrogen-containing organic molecules, as shown in Figure 4. The generated hydroxyl and other powerful oxidizing agents' radicals can efficiently degrade and mineralize these complex organic pollutants. The primary mechanisms by which AOPs target and eliminate organic nitrogen compounds include oxidation, hydroxylation, and fragmentation. These processes break down complex nitrogen-containing molecules into simpler, less harmful by-products such as nitrogen gas, carbon dioxide, and water. The application of AOPs for removing organic nitrogen compounds provides several advantages, including high efficiency, broad-spectrum activity, and the potential to mineralize pollutants into harmless end-products. However, challenges such as the high energy requirements and the need for catalysts in certain processes need to be addressed for widespread implementation. Additionally, the integration of AOPs with conventional treatment methods may enhance their overall efficiency and ensure the comprehensive removal of organic nitrogen compounds from wastewater.

Generation of Hydroxyl Radicals by Fenton's Reagent

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \dot{O}H + OH^- \tag{6}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + O\dot{O}H + H^+ \tag{7}$$

$$H_2O_2 \rightarrow \dot{O}H + O\dot{O}H + H_2O \tag{8}$$

Generation of Hydroxyl Radicals by Ozonation

$$O_3 + OH^- \rightarrow OOH^- + O_2 \tag{9}$$

$$O_3 + OOH^- \rightarrow O\dot{O}H + O_3^{\cdot -} \quad (10)$$

$$O_3^{\cdot -} + H^+ \rightarrow OO\dot{O}H \quad (11)$$

$$OO\dot{O}H \rightarrow \dot{O}H + O_2 \quad (12)$$

Generation of Hydroxyl Radicals by UV Light (Homolytic Cleavage)

$$H_2O_2 + UV \rightarrow 2\dot{O}H \quad (13)$$

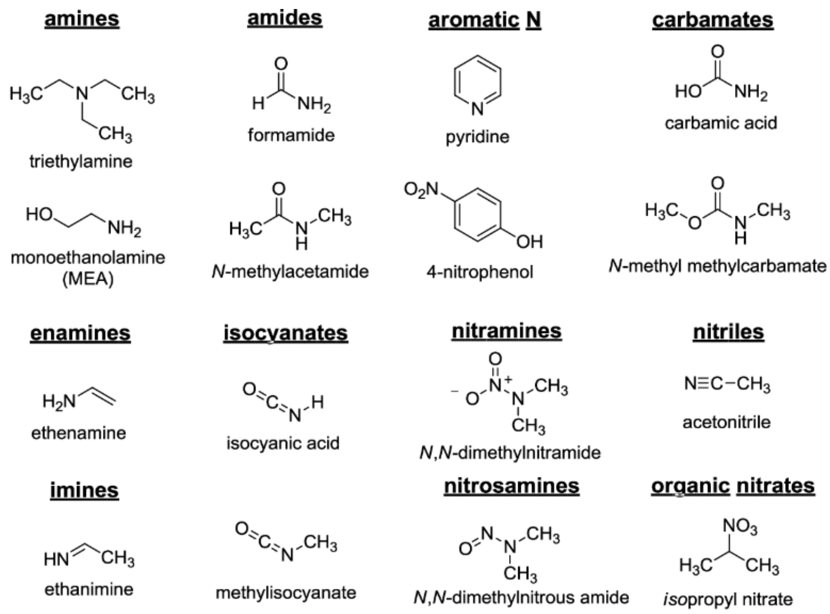

Figure 4. Some common examples of organic nitrogen compounds [136]. Reprinted with permission from reference [136], 2024, Nadine Bordaus-Dedekind.

Although the hydroxyl radical is the strongest oxidant applied for complete conversion, there are other options. For example, sulfate-based oxidants have been shown to be able to oxidize amino compounds [137]. Chen & Huang [138] conducted a study highlighting persulfate's capability in decomposing aniline within synthetic wastewater. They compared its performance with an electrolysis-supported persulfate treatment, wherein electrolysis enhances the medium with oxidative species derived from the reduction of oxygen and the oxidation of water. When evaluated under similar conditions and after a 7-h batch operation, electrolysis–persulfate demonstrated a $\%RE_{TOC}$ approximately three times higher (55%) than the individual processes alone. This outcome suggests a synergistic relationship, which the authors attribute to the generation of more potent sulfate oxidants through the reduction of persulfate in the solution. The elevated removal rates were achieved at a higher pH, temperature, persulfate concentration, and electrode potential. The optimal conditions, for complete TOC removal at a nitrogen dosage of 150 mL/min, were determined to be a pH of 3, temperature of 318 K, persulfate concentration of 3 wt%, and electrode potential of 6 V. Additionally, Krysova et al. [139] investigated the kinetics of diuron photocatalytic degradation utilizing TiO_2. They formulated a kinetic model to describe the involved reactions and the generation of intermediates. The study's findings indicate that the presence of Q-TiO_2 in the solution resulted in the photocatalytic degradation of approximately one-third of the diuron molecules to aliphatic side chains. Meanwhile, another two-thirds were degraded by the hydroxyl radical, which attacks the benzene ring and causes its breakage.

Chlorination was effectively employed to remove nitrogen compounds, particularly ammonia, from wastewater [140–142]. Chlorine undergoes a reaction in water, leading to the formation of hypochlorous acid (HOCl), which later on dissociates into hypochlorite

(OCl-). In the first place, these components serve as the primary disinfectants. In addition, HOCl reacts with ammonia in a sequence reaction, converting it to elemental nitrogen, nitrites, and nitrates following breakpoint chlorination. The breakpoint chlorination marks the stage at which any additional chlorine remains in the form of free chlorine, indicating the absence of further oxidizable substances for it to react with.

$$HOCl + NH_3 \rightarrow N_2 + NO_2{}^- + NO_3{}^- + HCl \quad (14)$$

Devi & Dalai [143] investigated the rates of formation and decay of chloramine intermediates, which are implicitly present in Equation (14), following breakpoint chlorination in brine solutions. They concluded that NCl_3, the ultimate intermediate capable of reacting with hypochlorous acid to produce final products, becomes the preferred product at low pH and high Cl_2/NH_3 ratios. Conversely, higher pH values favor NH_2Cl and $NHCl_2$. This information holds significant implications for the parameters of the ammonia removal process. The pH levels need to be sufficiently high to shift Equation (5) to the left, ensuring the maximum ammonia can react with HOCl. However, the pH also must be low enough to promote trichloramine generation, thereby favoring the evolution of nitrogen gas. In addition to the conventional reaction of ammonia with HOCl to yield nitrogen gas, HOCl and OCl^- are by themselves oxidizers, as is illustrated by Yao et al. [144]. In their study, they have shown that combining the breakpoint chlorination process with electrochemical conversion could convert nitrates to $NH_4{}^+$ at the cathode. Moreover, the ammonium ion is later oxidized by OCl^-. This combined process was able to yield a complete conversion of $NO_3{}^-$ to N_2 with the addition of Cl^-.

Nitrogen removal can be achieved partially or nearly completely through struvite precipitation [145–147]. Although typically used for phosphorus removal from wastewaters, this process also targets nitrogen as ammonium. It involves a reaction facilitated by magnesium ions, leading to the formation of struvite crystals, which can be efficiently filtered out:

$$Mg^{-2} + NH_4{}^+ + PO_4{}^{-3} \rightarrow MgNH_4PO_{4(s)} \quad (15)$$

Shu et al. [19] employed a process that aimed to remove manganese and ammonia from manganese-rich mining leachate through carbonate and struvite precipitation. It was shown that the maximum $\%RE_{NH4}$ of 97.4% was observed at a pH and P:N ratio of 9.5 and 1.1, respectively. A further increase in pH decreased the $\%RE_{NH4}$, most likely due to the shifting of the ammonia/ammonium equilibrium (reaction in Equation (5)) to the left. Also, an economic analysis showed that the cost of the treatment process was 7.5 USD/m^3. Due to its low cost, it was proposed that this process could be an economic approach to achieve significant TAN removal from coking wastewater using a decomposed struvite recycling stream [22]. In this recycling process, struvite crystals are broken down using calcium hydroxide, followed by high-quality gypsum by adding sulfuric acid to the solution. Utilizing this combination, an anticipated removal of up to 89% of TAN was expected when recycling struvite at a pH of 9.5. The experimental results closely aligned with this expectation, measuring an actual removal rate of 86%. The cost analysis for struvite precipitation, considering TAN removal with and without recycling and pretreatment, revealed values of USD 0.55 and USD 2.05 per cubic meter of coking wastewater, respectively. Similarly, in the treatment of swine wastewater, a dual approach involving struvite electrochemical precipitation and the recycling of a non-ammonia-containing struvite electrolysis product has been applied to concurrently remove phosphorus and ammonia nitrogen. The electrochemical precipitation method, coupled with recycling, was projected to eliminate over 90% of TAN from the wastewater, a prediction substantiated by an experimental determination of 93%. Effective statistical analysis is imperative for optimizing nitrogen removal, as exemplified in the established research. In one instance, response surface methodology (RSM) was employed to maximize ammonia nitrogen removal from vanadium-extracted effluent while minimizing the presence of Cr(VI) in the crystals. RSM identified optimal conditions, including a pH value of 9.16 and Mg/N and P/N ratios of 1.3 and 1.165, respectively.

These conditions resulted in an impressive $\%RE_{NH4}$ of 98.87%. Table 5 outlines the most recent successful implementations of physico-chemical technologies for the treatment of nitrogen-rich wastewater.

Table 5. Reported research on the application of physico-chemical treatment of nitrogen wastewater.

Process	Wastewater Type/Source	Nitrogen Content (mg/L)	Nitrogen Cleaner/Consumer	Nitrogen Removal Rate/Capacity	Reference
Air Stripping	Municipal wastewater	61.04 NH_4^+	Air	91% NH_4^+	[31]
	Swine wastewater	1308 ± 142 TAN		79.7 ± 16.8% TAN	[36]
	Synthetic wastewater	1000 mg/L NH_3-N		37% TN	[94]
		1000 NH_3		94.3% NH_3	[100]
Adsorption	Domestic sewage wastewater	168.87 NH_4^+	Bentonite modified with aluminum and tannin	>75% NH_4^+-N	[26]
	Landfill leachate	790 NH_3	Activated carbon modified with organic acid	94.30% NH_3 3.063 mg/g	[30]
	Landfill leachate	600.18 ± 16.18 NH_4^+-N	Natural zeolite clinoptilolite	>90% NH_4^+-N 3.59 mg/g	[29]
	Sewage wastewater	9.30 ± 3.28 NH_4^+-N	Bio-ceramic modified with Zn and Fe	~43% NH_4^+-N	[17]
	Swine wastewater	400 TAN (Synthetic) 108 TAN (Real)	Natural zeolite clinoptilolite	14–16 mg/g (Synthetic) 9.81 mg/g (Real)	[38]
	Synthetic wastewater	~1000 TAN	Iron-loaded activated carbon	31% TAN 0.15 mg/g	[104]
		6.5 NH_4^+-N	Natural zeolite–rice straw	49–78% NH_4^+-N 40–66% TN	[107]
		6.5 NO_3^--N		68–83% NO_3^--N 46–62% TN	[107]
		1000 NH_4^+	Lithium titanate (LiT)	~90% NH_4^+	[110]
		5000 NH_4^+-N	Granular ceramic from volcanic ash	19.44% NH_4^+-N	[106]
Ion Exchange	Municipal wastewater	0.006–26 NH_4^+-N	Synthetic zeolite $K_{12}Al_{10}Si_{10}O_{40}Cl_2 8H_2O$	28–96% NH_4^+-N 0.9–17.1 mg/g	[33]
	Synthetic wastewater	40 NH_4^+	Natural Si–Al Yemeni zeolite	99% NH_4^+ 11.8 mg/g	[114]
Membrane Technology	Landfill leachate	2547 ± 270 NH_3-N	Polypropylene	98% NH_3	[28]
	Synthetic wastewater	400 NH_3	Polar carboxylated carbon nanotubes	14% NH_3	[117]
	Domestic–blackwater wastewater	46–62 TN	N.A *	79% TN	[27]
	Space habitation wastewater	540–5100 TN	Siloxane tubes/Nitrosomonas, Nitrosospira, Nitrobacter, and Nitrosococcus	30–70% ON	[35]
	Swine wastewater (liquid digestate)	564.50 ± 7.07 TN 532.36 ± 5.24 NH_4^+-N	Polypropylene/polyethylene/ polyphthalamide/bacteria	95% TN	[40]
	Synthetic wastewater	10–60 NA 53.27–79.85 TN	Silicon rubber–epoxy resins/proteobacteria and bacteroidetes	98% NA 88.52% TN	[18]
	Urine wastewater	565–1030 NH_4^+-N	N.A	36% TN 61–70% NH_4^+-N	[41]

Table 5. *Cont.*

Process	Wastewater Type/Source	Nitrogen Content (mg/L)	Nitrogen Cleaner/Consumer	Nitrogen Removal Rate/Capacity	Reference
Chemical Treatment	Coking wastewater	535 ± 29 TAN	Struvite precipitation	86% TAN	[22]
	Manganese electrolysis leachate	823 ± 4.0 NH_4^+		97.4% NH_3-N	[19]
	Swine wastewater	426 ± 21 TAN		93% NH_3-N	[37]
	Synthetic wastewater	60 Aniline	Electrolysis–persulfate (AOP)	~100% TOC	[138]
	Synthetic wastewater	20 Roxarsone	Fenton (AOP)	75% TOC 50–64% EOC	[135]
	Synthetic wastewater	30 NO_3^--N	Breakpoint chlorination (HOCl)	~100% NO_3^--N	[144]
	Vanadium-extracted effluent	2850 ± 84 NH_4^+-N	Struvite precipitation	98.87% NH_3-N	[42]

* Not available/mentioned.

6. Shortcomings and Future Directions and Recommendations

Although several studies have primarily examined the broad elimination of nitrogen from wastewater, research work that focuses on addressing the removal of distinct nitrogen molecules (e.g., ammonia, nitrate, and nitrite) on an individual basis is limited. To handle these issues effectively, it is necessary to adopt a comprehensive and cooperative strategy that integrates technological improvements, environmental impact assessments, and a strong emphasis on resource recovery. It is required that the future of nitrogen-rich wastewater treatment has the potential to be more effective, sustainable, and environmentally friendly by adopting innovation and interdisciplinary applications. The limitation of past work in terms of nitrogen removal from wastewater can be summarized as follows.

1. Excessive focus on traditional treatment approaches: Most of the previous studies have frequently utilized conventional treatment approaches, such as activated sludge procedures and biological nutrient removal, without investigating novel technologies that can be used to target specific nitrogen components in wastewater. This could potentially impede the effectiveness and long-term viability of nitrogen removal.
2. Lack of a thorough assessment of the environmental consequences: Past studies have failed to include the possible ecological consequences of nitrogen removal operations, such as the production of detrimental by-products or the carbon emissions linked to energy-intensive techniques.
3. Lack of effective incorporation of cutting-edge technologies: The utilization of cutting-edge technology, such as membrane bioreactors, electrochemical approaches, or new biological processes, has been restricted. Subsequent investigations should delve into the capabilities of these technologies to enhance the efficiency of nitrogen removal.
4. Lack of attention to opportunities for resource recovery: Numerous studies have failed to consider the possibility of extracting useful nutrients or energy from nitrogen-rich wastewater, hence neglecting the potential for resource recovery. This omission signifies a lost chance to implement sustainable methods of treating wastewater.

Based on the previous comments, the following action plan is proposed for subsequent advancement.

1. In-depth knowledge of nitrogen forms: Future studies should focus on comprehending and addressing distinct nitrogen forms independently, considering the distinct difficulties related to the elimination of ammonia, nitrate, and nitrite.
2. Investigation into cutting-edge treatment technologies: Researchers should assign greater importance to the investigation of cutting-edge technologies, such as mem-

brane processes, electrochemical methods, and nature-inspired treatment approaches, to improve the effectiveness and long-term viability of nitrogen removal.
3. Comprehensive environmental impact assessment: Future research should do thorough environmental impact evaluations, considering the life cycle analysis of nitrogen removal techniques to detect and address any potential environmental disadvantages.
4. Smart monitoring and control systems integration: By implementing intelligent monitoring and control systems, it is possible to optimize nitrogen removal operations in real time, resulting in improved efficiency and decreased operational expenses.
5. Emphasize the utilization of resources and the implementation of a circular economy: Research endeavors should focus on investigating possibilities for extracting resources from wastewater that contains high levels of nitrogen, thus aiding in the advancement of a circular economy within the field of wastewater treatment.

Implementing these recommendations in future research can rectify the limitations of previous studies and enhance the efficacy, durability, and eco-friendliness of nitrogen-rich wastewater treatment methods.

7. Conclusions

This comprehensive analysis emphasizes the importance of microbial processes in the elimination of nitrogen from wastewater. The simultaneous nitrification–denitrification process (SNDP) and the anammox process are emerging as potential methods, with significant rates of elimination. The study highlights the impact of microbial communities, specifically their reactions to different conditions like salinity and the introduction of graphene derivatives, in improving nitrogen removal. Moreover, the mutually beneficial association between bacteria and microalgae highlights a decrease in the need for oxygen and carbon, hence enhancing the efficiency of nitrogen removal. Fluidized bed biofilm reactors are quite effective in accomplishing the SNDP. The findings aid in the continuous endeavors to enhance and optimize microbial-based technologies for sustainable nitrogen removal, providing resolutions to tackle environmental concerns linked to nitrogen-rich wastewater. Suspended growth bioreactors are becoming increasingly recognized as highly promising systems for nitrogen removal due to their straightforward design and cost-effectiveness. The bioreactors demonstrate their adaptability by effectively accommodating a range of microbial activities, such as anoxic and aerobic phases, anammox, and simultaneous nitrification–denitrification (SND). Noteworthy findings reveal a strong inclination towards low COD/N ratios, highlighting the potential of these bioreactors to adjust to various wastewater conditions. The incorporation of comammox bacteria into an anammox-dominated up-flow anaerobic sludge blanket (UASB) bioreactor demonstrates a beneficial effect on the elimination of total inorganic nitrogen (TIN). Moreover, the incorporation of magnetic microparticles highlights improved efficiency and simplified extraction. Furthermore, immobilized growth systems offer various advantages, such as enhanced treatment efficiency and the ability to introduce beneficial microorganisms, which make them effective tools for environmental cleanup. Examining instances such as MBBRs, bioaugmented sludge, and hybrid biocarriers offers a valuable understanding of how these systems can adapt to several types of wastewater. The choice of biocarrier materials, together with fine-tuned process parameters, becomes a crucial element in attaining optimal performance. Using innovative technologies, such as the integration of membranes and microbial electrochemical cells, expands the range of immobilized growth systems for nitrogen removal. Air stripping treatment, despite its disadvantages, demonstrates efficient removal of nitrogen from wastewater. Cost-effective solutions such as innovative pretreatment and high-frequency electric fields, such as microwaves, are available. The utilization of activated carbon and zeolites, together with alternative substances like bentonite, has notable efficacy in removing contaminants, especially when supplemented with enhancements such as iron loading or the application of organic acids. Zeolites, specifically, exhibit potential for the effective treatment of swine wastewater. Ion exchange is a promising technique for the removal of ammonium, nitrite, and nitrate ions, demonstrating its adaptability in treating various nitrogen-containing substances. Variables such as pH, the amount of adsorbent used, and the duration of contact have significant impacts on the effectiveness of these physico-chemical techniques. Membrane technologies and chemical treatments, such as advanced oxidation processes (AOPs), exhibit a notable capacity for efficiently removing nitrogen. Successful nitrogen removal requires the integration of several methods, optimization of critical parameters, and consideration of techno-economic considerations. Further investigation should focus on investigating the combined effects of various methods and tackling new obstacles to improve the overall efficiency of nitrogen removal procedures, thus guaranteeing the sustainable and eco-friendly treatment of wastewater.

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