Engineered Solutions for a Greener Future: Advancing Nitrate Removal Technologies in Aquatic Systems

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Abstract: Nitrate, as a common pollutant in surface water and groundwater, not only causes aquatic ecosystem problems such as eutrophication of water bodies, but also poses a threat to human health. This article reviews various treatment technologies for nitrate wastewater, covering three methods: physical, chemical and biological. Among them, the denitrification process is one of the effective ways to treat wastewater with a low carbon-nitrogen ratio and has significant advantages. This paper first systematically introduces the principles and applications of various methods for treating nitrate wastewater, with a focus on discussing the good performance of different methods in the nitrate removal process and the key strategies to improve their removal efficiency. Finally, a comprehensive summary of various methods was conducted, and prospects were made for the existing problems and future research directions, aiming to provide a theoretical basis and reference for the efficient removal of nitrate in water bodies.

Keywords: Nitrate Wastewater; Denitrification; Physical Treatment Technology; Chemical Treatment Technology; Biological Treatment Technology

1. Introduction

In recent years, with the rapid development of industry and agriculture, nitrate levels in groundwater and surface water have exceeded safety limits, with pollution severity increasing annually. Nitrate contamination has emerged as a globally pressing environmental issue, whose widespread presence poses significant threats to ecosystems and human health. It not only induces eutrophication in rivers, lakes, and coastal areas but also enters the human body through tap water or plant accumulation. Nitrate may react with amines or amides in the body to form nitrosamines, which have been confirmed as carcinogenic and teratogenic agents, potentially causing cancer, birth defects, or other adverse health effects [1]. For instance, health issues such as methemoglobinemia, diabetes, spontaneous abortion, thyroid diseases, and gastric cancer have been linked to nitrate exposure. Infants under six months are particularly vulnerable to methemoglobinemia from excessive nitrate intake, which can reduce blood oxygen levels and even threaten their lives.

Overall, effective strategies are urgently needed to control nitrate pollution. Current treatment methods for nitrate contamination in water bodies primarily include physical, chemical, and biological approaches. Physical technologies for nitrate removal mainly include adsorption [2], ion exchange, reverse osmosis, and electrodialysis. Chemical methods encompass metal reduction, catalytic reduction, and electrochemical reduction. Biological treatments are dominated by biological denitrification, a critical process for nitrogen removal in wastewater treatment plants. Compared with physical and chemical techniques, biological denitrification offers notable advantages such as low cost, simple operation, and zero pollution, making it the most widely adopted method. This paper systematically reviews the principles and application cases of nitrate removal technologies in water bodies, analyzes the application characteristics and limitations of various methods, and discusses future research directions.

2. Physical Treatment Technologies

2.1 Adsorption

Adsorption relies on the capacity of adsorbents to attract solutes from gaseous or liquid phases, concentrating contaminants onto the adsorbent surface. Nitrate removal via adsorption hinges on the interaction between nitrate nitrogen and the adsorbent, facilitating the transfer of nitrate from the aqueous phase to the adsorbent interface. Agricultural waste-derived adsorbents have garnered significant attention recently due to their broad applicability, environmental benignity, and waste-recycling potential [3]. The efficacy of adsorption fundamentally depends on selecting appropriate adsorbent materials, which can capture soluble pollutants at the interface. Common adsorbents for nitrate removal include carbon-based materials, organic polymers (e.g., chitosan), bamboo charcoal powder, hydroxyapatite, and agricultural residues.

2.2 Ion Exchange

Ion exchange operates via the exchange of ions between the solution and ion exchange resins. Strong-base anion exchange resins are widely employed for nitrate-laden water treatment, valued for their rapidity, high efficiency, stability, and operational simplicity—making them ideal for nitrate removal in small-scale wastewater systems. However, ion exchange resins suffer from issues such as cumbersome operation, high dosage requirements, and prone scaling. Zhu Jing et al. studied nitrate removal using prepared macroporous anion resins and found that the nitrate removal rate reached 50% at 10 minutes, with the optimal aspect ratio of the fixed bed being 20, and the treatment effect stabilized at 30 minutes. Huang Junliang et al. treated raw water from a reservoir using the ion exchange method under optimal operating conditions: a filtration rate of 6 m/h, a 10% (mass fraction) NaCl solution as the regenerant, a regenerant volume three times that of the resin, and a regeneration process lasting 2 hours, with regeneration efficiency stably maintained at 85%-90%.

2.3 Reverse Osmosis

Reverse osmosis is a separation technology leveraging the selective permeability of semipermeable membranes. By applying pressure to one side of the solution, water molecules are driven through the membrane while other substances are retained on the membrane surface, effectively removing contaminants. Maghsudi et al. [4] reported 98.9% nitrate removal efficiency via reverse osmosis treatment of municipal wastewater pretreated with activated carbon. Sewak et al. [5] achieved 78% nitrate removal from groundwater using reverse osmosis. Compared to other processes, reverse osmosis features simple equipment, ambient-temperature operation, wide applicability, small footprint, high effluent quality, and high automation. However, it suffers from high energy consumption, requires secondary treatment of concentrated wastewater, and lacks ion selectivity.

2.4 Electrodialysis

Electrodialysis (ED) employs a direct current (DC) electric field as the driving force and relies on the selective permeability of ion exchange membranes to efficiently separate electrolyte ions from aqueous solutions and other non-charged components. This method offers significant advantages, including no requirement for external chemical addition, low cost, and high selectivity. Jingjing et al. reduced nitrate concentration from 443 mg/L to 9 mg/L through ED experiments. Gu et al. [6] demonstrated in ED ion exchange membrane bioreactor experiments for nitrate removal that a removal efficiency of 98.94% was achieved at a nitrate concentration of 40 mg N/L, a voltage of 5 V, and a biomass concentration of 3.00 g VSS/L. Compared with reverse osmosis (RO), ED is less sensitive to membrane fouling and scaling. Therefore, ED not only achieves higher recovery rates but also minimizes the difficulty of brine treatment.

3. Chemical Treatment Technologies

3.1 Metal Reduction

Metal reduction methods employ metallic elements such as Fe, Al, and Cu as reductants. Reductive iron powder is frequently used in chemical treatments for nitrate-contaminated water due to its high reducibility, low cost, and minimal environmental impact. For example, Zhao Shuang et al. demonstrated in experiments using zero-valent iron (ZVI) to treat low-concentration nitrate wastewater that when the NO_3^- concentration was 50 mg/L and pH was 2, adding 10 g/L ZVI to the reaction system and reacting at 50°C for 2 hours, followed by adding 300 mmol/L sodium hypochlorite (NaClO), reduced the effluent NO_3^- concentration to <5 mg/L and NH_4^+ to <2 mg/L. Dong et al. used modified attapulgite-supported nano-zero-valent iron (NZVI) to treat nitrate nitrogen in groundwater, achieving a final removal efficiency of ~83.8% at an initial pH of 7.0. Liu Yanlan et al. employed a Zn/Ag bimetallic system to reduce NO_3^- to NO_2^-, followed by deep reduction of NO_2^- to N_2 using sulfamic acid, achieving a nitrate reduction rate of 93.2% with only 3.9% ammonia nitrogen formation.

3.2 Catalytic Reduction

In the presence of supported metal catalysts, reducing agents such as H_2, HCOOH, and CH_3OH are used for nitrate reduction. The catalytic reduction of NO_3^- is highly influenced by catalyst loading and NO_3^- concentration. Higher catalyst loading generally leads to higher NO_3^- removal efficiency at the same nitrate concentration. For example, Al Bahri et al. demonstrated that in 2.5% Cu-Pd/NZVI catalysts, increasing the Pd concentration from 1 wt% to 5 wt% enhanced NO_3^- removal efficiency from 75% to nearly 100%. Choi et al. achieved the highest nitrate (50 ppm) removal efficiency using Pd:Cu/λ-Al_2O_3 as the catalyst and formic acid as the reductant, under conditions of a 4:1 Pb/Cu ratio, 0.75 g/L catalyst dosage, and 2-fold excess formic acid. Miranda Zoppas et al. [7] synthesized a (Pd, In)-based catalyst with 1 wt% Pd and 0.25 wt% In supported on alumina, showing that formic acid as the reductant at pH 4.0–5.0 significantly enhanced nitrate reduction kinetics.

3.3 Electrochemical Reduction

Electrochemical reduction primarily occurs via two mechanisms: direct reduction and indirect reduction. Typically, NO_3^- reduction reactions take place at the cathode surface, with reduction products mainly including NO_2^-, N_2, and NH_4^+, alongside possible byproducts such as NO_2, NO, N_2O, NH_2OH, and N_2H_4 [8]. In experiments by Chauhan et al., aluminum served as the cathode and Ti/RuO_2 as the anode for electrochemical nitrate reduction and anodic ammonium ion oxidation. Under conditions of 100 mg/L NO_3^-, 300 mg/L NaCl, a current density of 333.3 $A\cdot m^{-2}$, and pH 6 for 120 min, 95% of NO_3^- was converted to N_2. Su et al. [9] investigated bimetallic palladium (Pd) and tin (Sn) catalysts electrochemically deposited on stainless steel mesh supports (Pd-Sn/SS) for selective NO_3^- conversion to N_2 gas. Results showed that electrodes prepared with a Pd:Sn molar ratio of 1:1 exhibited a high nitrate conversion efficiency (95%), outperforming many literature reports. Electrocatalytic reduction technology has garnered significant attention due to its advantages of minimal or no reagent addition, controllable byproducts, small footprint, and ease of automation.

4. Biological Treatment Technologies

4.1 Heterotrophic Denitrification

The efficient operation of heterotrophic denitrification processes critically relies on ensuring the influent contains abundant biodegradable carbon sources. Commonly used solid-phase carbon sources include natural cellulosic materials such as corn cobs, rice husks, crop straws, and wood chips, as well as synthetic degradable polymers like polycaprolactone (PCL), polylactic acid (PLA), polyhydroxyalkanoates (PHAs), and polybutylene succinate (PBS). Liang et al. applied crop straws and wood chips as external carbon sources in denitrification reactors and observed that straws yielded the optimal denitrification performance at a hydraulic retention time (HRT) of 24 hours. Zhong Hua et al. utilized corn cobs as solid-phase carbon sources in denitrification systems and demonstrated that corn cobs, serving as slow-release carbon sources coupled with biofilm carriers, facilitated microbial attachment and growth, thereby achieving effective nitrogen removal. Chu et al. employed PCL-filled fixed-bed bioreactors for NO_3^- removal from groundwater, achieving an average effluent NO_3^- concentration below 3.70 mg/L, a total nitrogen (TN) removal efficiency exceeding 95% at HRT of 3–6 hours, and maintaining low levels of NO_2^- (<0.32 mg/L) and NH_4^+ (<0.78 mg/L). Xu et al. enhanced the TN removal rate to 67.65% by introducing microwave-alkali-treated excess sludge hydrolysate as an external carbon source into an AAO-MBR reactor. While heterotrophic denitrification is characterized by rapid reaction kinetics and high nitrogen removal efficiency, with widespread applications in municipal wastewater treatment, challenges remain in precise carbon source dosing and managing excessive sludge production due to the rapid growth and metabolism of heterotrophic bacteria. These challenges give rise to the formation of biological flocs and reaction byproducts, necessitating secondary treatment for residual sludge disposal.

4.2 Autotrophic Denitrification

Autotrophic denitrification technology using inorganic carbon as the substrate has become a research hotspot due to its independence from organic carbon sources and the low production of excess sludge resulting from the generally slow growth rate of autotrophic bacteria [10]. Depending on the type of electron donor, autotrophic denitrification can be classified into four categories: hydrogenotrophic, ferriautotrophic, thioautotrophic, and sulfur-iron autotrophic denitrification.

4.2.1 Hydrogenotrophic denitrification

In the hydrogenotrophic denitrification process, hydrogenotrophic denitrifying bacteria utilize H_2 as the electron donor and NO_3^-/NO_2^- as electron acceptors to perform denitrification, with the products being N_2 and H_2O. The reaction is represented by equation (1):

$$5H_2+2NO_3^-+2H^+\rightarrow N_2+6H_2O \qquad (1)$$

The H_2-driven denitrification technology features advantages including high removal efficiency, low energy consumption, no harmful byproducts, and independence from external organic carbon sources. When Vasiliadou et al. applied hydrogenotrophic denitrification in a continuously operated packed-bed reactor for nitrate removal from drinking water, the reactor achieved a maximum denitrification rate of 6.2 g NO_3^--N/L/d. However, external hydrogen supply poses safety risks and suffers from low utilization efficiency.

4.2.2 Thioautotrophic denitrification

Thioautotrophic denitrification is a process where various reduced sulfur compounds and sulfides (S^0, S^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$) serve as electron donors, CO_3^{2-} or HCO_3^- act as inorganic carbon sources, the electron acceptor NO_3^- is reduced to N_2, and the reduced sulfur is oxidized to SO_4^{2-}. The reaction mechanisms are described by equations (2)–(5):

$$S^0+1.2NO_3^-+0.4H_2O\rightarrow SO_4^{2-}+0.6N_2+0.8H^+ \qquad (2)$$

$$S^{2-}+1.6NO_3^-+1.6H^+\rightarrow SO_4^{2-}+0.8N_2+0.8H_2 \qquad (3)$$

$$5SO_3^{2-}+2NO_3^-+H_2O\rightarrow 5SO_4^{2-}+N_2+2OH^- \qquad (4)$$

$$S_2O_3^{2-}+1.6NO_3^-+0.2H_2O\rightarrow 2SO_4^{2-}+0.8N_2+0 \qquad (5)$$

Thioautotrophic denitrification has attracted extensive attention due to its high nitrogen removal efficiency and carbon emission reduction capacity [11]. During the thioautotrophic denitrification process, the production of H^+ decreases the effluent pH, while significant amounts of SO_4^{2-} are generated. To address these challenges, some researchers have proposed adding appropriate amounts of limestone to the reaction system to regulate alkalinity, while others have suggested integrating thioautotrophic denitrification with other processes to overcome its limitations. For instance, Sahinkaya et al. developed a thioautotrophic denitrification membrane bioreactor that achieved 99.6% NO_3^- removal efficiency at an initial NO_3^- concentration of 25 mg/L. Woo et al. fabricated sulfur-based carriers composed of elemental sulfur, calcium carbonate, activated carbon powder, and sodium silicate, which serve as alkalinity supplements and electron donors for autotrophic denitrification, respectively. This system significantly reduced total nitrogen (TN) and NO_3^- concentrations, with a TN removal rate of up to 81.2%.

4.2.3 Ferriautotrophic denitrification

Ferriautotrophic denitrification is a process in which Fe^0 or Fe^{2+} act as electron donors, and NO_3^- or NO_2^- serve as electron acceptors to reduce them to N_2. In denitrification involving Fe^0, H^+ is consumed, causing the system pH to rise continuously and leading to NO_2^- accumulation. The autotrophic denitrification equations are as follows (6)–(9):

$$Fe^0+0.4NO_3^-+1.2H_2O\rightarrow Fe^{2+}+0.2N_2+2.4OH^- \qquad (6)$$

$$2Fe^0+2NO_2^-+2H_2O+2H^+\rightarrow 2Fe(OH)_3+N_2 \qquad (7)$$

$$Fe^{2+}+0.2NO_3^-+2.4H_2O\rightarrow Fe(OH)_3+0.1N_2+1.8 \qquad (8)$$

$$6Fe^{2+}+2NO_2^-+14H_2O\rightarrow 6Fe(OH)_3+N_2+10H^+ \qquad (9)$$

Commonly used electron donors for ferriautotrophic denitrification include nano zero-valent iron (nZVI), granular zero-valent iron powder, iron filings, and sponge iron, all of which exhibit strong reducibility. Lee et al. employed macroporous alginate substrates embedded with Fe^0 nanoparticles to remove NO_3^- from aqueous solutions, achieving over 96.5% NO_3^- removal within 30 minutes of reaction. Li et al. investigated the denitrification performance and microbial characteristics of sludge systems with and without sponge iron addition, reporting a ~43% enhancement in total nitrogen (TN) removal efficiency in the sponge iron-amended sequencing batch reactor compared to the conventional system. To address the limitations of hydrogenotrophic, thioautotrophic, and ferriautotrophic denitrification in wastewater treatment, researchers have proposed the sulfur-iron co-substrate autotrophic denitrification method, which can improve NO_3^- removal efficiency while reducing SO_4^{2-} and H^+ production.

4.3 Sulfur-Iron Co-Substrate Autotrophic Denitrification Technology

Currently, pyrite (FeS_2) and ferrous sulfide (FeS) are the focus of research on sulfur-iron co-substrate autotrophic denitrification. Iron-sulfur minerals as substrates enable high-performance autotrophic denitrification systems. Pyrite, composed primarily of FeS_2, theoretically provides both reduced sulfur and iron as electron donors to reduce NO_3^-. Electron transfer is mediated by enzymes secreted by autotrophic microorganisms, with inorganic carbon (e.g., CO_3^{2-}, HCO_3^-) utilized for cell synthesis, as described by reaction (10):

$$FeS_2+3NO_2^-+2H_2O\rightarrow Fe(OH)_3+2SO_4^{2-}+H^++1.5N_2 \quad (10)$$

Pyrite consumes minimal alkalinity during denitrification, offering buffering capacity to maintain system pH balance and generating low levels of SO_4^{2-}. Experimental findings by Torrentó et al. reveal that *Thiobacillus denitrificans* denitrifying bacteria can utilize pyrite as an electron donor for nitrate reduction, achieving 100% nitrate-nitrogen removal efficiency in long-term inoculated flow experiments. Liu et al. investigated pyrite-sulfur coupled autotrophic denitrification, reporting an effluent NO_3^--N concentration of 0.32±0.11 mg/L and an average total nitrogen (TN) removal efficiency of 99.14%.

Ferrous sulfide (FeS) represents the primary initial iron sulfide mineral, with subsequent sulfidation processes driving transformation into more stable phases (e.g., greigite) and ultimately culminating in pyrite formation. The reaction equation for FeS-based autotrophic denitrification is depicted in equation (1.11):

$$FeS_2+9NO_2^-+8H_2O\rightarrow 5Fe(OH)_3+5SO_4^{2}+H^++4.5N_2 \quad (11)$$

Huang et al. noted that ferrous sulfide (FeS) supports autotrophic denitrification more efficiently than pyrite, while releasing minimal free sulfide that could otherwise cause incomplete denitrification or ammonia formation. Ma et al. [12] investigated a novel FeS-driven autotrophic denitrification-anammox hybrid system, which achieved 100% NO_3^--N removal at a nitrogen loading rate of 0.20 g N/L/d over 120 days of operation. Zhou Xiang et al. experimentally demonstrated that *Thiobacillus denitrificans* ATCC 25259 can only utilize FeS as an electron donor for autotrophic denitrification-based nitrogen removal, using FeS as the primary substrate.

5. Conclusions and Perspectives

Nitrate pollution has emerged as one of the most critical water quality issues, posing severe threats to aquatic ecosystems and human health via drinking water safety concerns. Current treatment methodologies each exhibit distinct limitations: (1) Physical methods impose strict requirements on influent water quality and incur high operational costs, primarily applied in wastewater reuse, drinking water purification, and desalination. Despite high nitrate removal efficiency, these methods merely concentrate and transfer nitrates, risking secondary pollution. (2) Chemical reduction methods are constrained by secondary pollutant generation (e.g., ammonia nitrogen) and the need for rigorous pH control during reactions. (3) Biological denitrification, an economical and efficient approach to reduce NO_3^- to N_2, is favored for its high efficiency, low cost, and environmental friendliness, generating less sludge and secondary pollution while promoting sustainability. Although current research demonstrates promising nitrogen removal performance of biological denitrification technologies, their underlying reaction mechanisms require further in-depth investigation.

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