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Review

Nitrate-Polluted Waterbodies Remediation: Global Insights into Treatments for Compliance

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Featured Application: Nitrate pollution in waterbodies is a topic of environmental and health concern. Being aware of the wide range of technologies available is a challenge of real interest that will facilitate the selection of an eco-friendly and affordable water treatment technology in terms of equipment investment and energy costs.

Abstract: Nitrate (NO_3^-) pollution of surface and groundwater bodies is a global problem of increasing concern, which has stimulated significant research interest. Nitrogen is crucial for life as a macronutrient for living organisms on Earth, but the global nitrogen cycle has been seriously altered by intensification of human activities, leading to eutrophication and hypoxic conditions of aquatic ecosystems. Due to nitrogen overfertilization, intensive agricultural practices generate huge nitrate fluxes that inadvertently deteriorate water quality. Different industrial processes also contribute to NO_3^- pollution in the environment. There are multiple technologies capable of achieving effective denitrification of waterbodies to ensure safe NO_3^- levels. Either separation-based or transformation-based denitrification technologies must address the challenges of by-product generation, increased energy demand, and reduced environmental footprint. This paper highlights the most used approaches, along with some promising alternatives for remediation of nitrate-polluted waters.

Keywords: nitrate pollution; waterbodies; remediation; denitrification; removal technologies

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1. Introduction

Water is essential for economic growth, human health, and the environment. In terms of quantity and quality, freshwater is a limited resource on Earth. The pollution of surface and groundwater poses a threat to aquatic ecosystems and society. The challenge of providing quality water, both for human consumption and for food production and recreational use, is undoubtedly one of the most pressing of the 21st century. Global warming, desertification, and the contamination of surface and groundwater have drastically reduced the availability of freshwater [1], and it is a key issue in meeting the Sustainable Development Goals (SDG) included in the 2030 Agenda for Sustainable Development, adopted by all United Nations Member States [2,3].

Nitrogen compounds in the soil may have a natural origin where they are subsequently oxidized to nitrates. Nitrate ions, driven by its extreme water solubility and resistance to fixation by soil colloids, are very susceptible to contamination by leakage. They can be easily washed into deep areas of the soil by rainfall and/or overirrigation, reaching groundwater bodies [4].

Diffuse agricultural pollution is the contamination of water, soil, and air, as a result of farming practices. This pollution depends on what happens on the Earth's surface and practically affects large areas of our planet. It is very significant in many world regions because of the cumulative effect that certain discharges can have on the environment. Agricultural practices such as seedbed preparation, ploughing, fertilization, slurry application, and crop spraying are all possible contributors to diffuse pollution [5,6]. Thus, there is a wide range of potential sources of diffuse pollution that are linked to agricultural practices and that can damage the environment. This diffuse pollution is particularly evident in water bodies, when due to rainfalls and the way the land is managed, nutrients, pesticides, faecal bacteria, chemicals, and fine sediments are leached from the land into streams, rivers, lakes, and groundwater.

European legislation, in the form of the Water Framework Directive 2000/60/EC of the European Parliament and of the Council, of 23 October 2000, highlights the issue of diffuse pollution [7]. Its main topic is integrated water management, and its primary objectives are to prevent degradation, and restore and improve surface and groundwater to reach and preserve their healthy ecological balance. Agriculture can lead to serious environmental impacts, sometimes difficult to quantify, on the surrounding waterbodies [8,9]. Within this European framework, different proposals are put forward, such as the so-called "from farm to fork", aligned with the Biodiversity Strategy for 2030, included in the European Green Deal, which contribute to tackling this problem. These lines of action set, among other objectives, a 50% reduction in excess nutrients, which will entail a 20% reduction in the use of fertilizers. The targets set by the Member States with these goals must be reached by the end of 2030, within a period close to the end of 2027, set as the deadline for achieving the environmental objectives in waterbodies [10].

By reason of its inherent nature, the effective nitrate pollution control and management is not simple and demands accurate analysis and insight into a variety of anthropogenic and natural processes. One of the effects of modern agriculture is the excessive use of fertilisers and manure, which causes high levels of certain nutrients, particularly phosphorus and nitrogen, to be transferred to waterbodies through diffuse processes [11]. Overconcentration of these nutrients in water leads to harmful impacts by promoting eutrophication, resulting in the consequent loss of both animal and vegetal species. The presence of nitrate in waterbodies is a consequence of the natural nitrogen cycle; the problem is that in certain areas, there has been an alteration of this cycle, causing an increase in the concentration of nitrates, mainly due to the excessive use of fertilizers and their subsequent run-off by rainwater or irrigation [12].

Excessive nutrient inputs (typically nitrates and phosphates) into the water and exposure to solar radiation promote excessive growth of organic matter and the development of phytoplankton, algae, and other green plants [13]. The proliferation of these organisms is the early stage of eutrophication; it causes a turbidity in the water, resulting in a murky green colour that prevents light from penetrating to the bottom of the ecosystem, and the vegetation is unable to photosynthesize and dies. Bacteria and other microorganisms feed on the dead matter, depleting the levels of dissolved oxygen in the water. This hypoxia causes fish kills, inhibits the development of other living organisms, and leads to the development of toxic and hazardous substances that compromise human health [14,15].

The concern is not only in the environment, but nitrate can also constitute a severe hazard to human health. Nitrate is non-toxic to human health. In fact, it has a positive protective effect on the stomach and an antimicrobial effect on gut pathogens. When the amount of nitrate is elevated, some of it may be converted into its harmful metabolites (nitrite ions) by bacterial reduction during food processing or intestinal transit. The ingestion of water with excessive nitrate concentrations disables human erythrocytes as oxygen carriers, especially in children, causing a fatal condition of methemoglobinemia [16,17]. Nitrate may also be responsible for the synthesis of N-nitrosamines and N-nitrosamides, with potential carcinogenic effects [18,19]. As a result of this background, there is concern among major international organizations such as the World Health Organization (WHO) and the Council of European Union that have set a limit on NO_3^- concentration in drinking water of 50 mg/L [20]. The quality standard of the Food and Agriculture Organization of the United Nations (FAO) in water for irrigation is a level of $NO_3^- < 22$ mg/L for unrestricted use, and with a slight to moderate degree of restriction, if the concentration ranges from 22 to 133 mg/L [21].

Reducing nitrate pollution is therefore a key issue, and this requires restoring the balance of the nitrogen cycle to achieve improvements in water quality [22]. Therefore, it is of great interest to adequately minimize diffuse pollution from agriculture and further integrate nutrient control technologies to limit eutrophication and protect the water environment [23]. This paper takes an in-depth look at the current leading technologies and some recent alternatives for remediation of nitrate-polluted waters. The aim is to provide a thorough knowledge of modern control technologies for the effective environmental remediation. The challenge is to find cost-efficient and energy-efficient technologies that will be both economically and environmentally sustainable.

2. The Biological Nitrogen Cycle

The nitrogen cycle is the biogeochemical loop that supplies nitrogen to living organisms and keeps it recirculating in the biosphere (Figure 1). Nitrogen undergoes a variety of chemical reactions (oxidations and reductions) (Table 1) that produce N-compounds with oxidation states ranging from +5 (NO_3^-) to −3 (NH_4^+) [24].

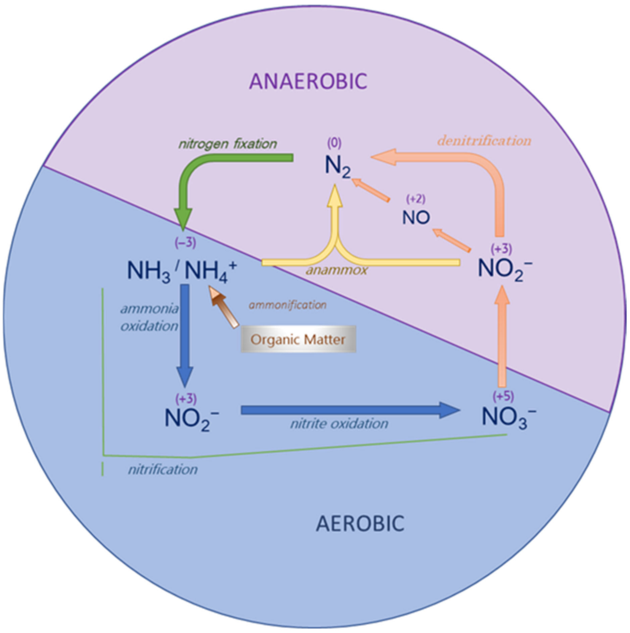


Figure 1. The biological nitrogen cycle.

Table 1. Chemical reactions in the nitrogen cycle.

Process	Chemical Reaction
■ Nitrogen fixation	$N_2 + 8\,H^+ + 8\,e^- \rightarrow 2\,NH_3 + H_2$
■ Ammonia equilibrium	$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$
■ Ammonium oxidation	$NH_4^+ + 3/2\,O_2 \rightarrow NO_2^- + H_2O + 2\,H^+$
■ Nitrite oxidation	$NO_2^- + 1/2\,O_2 \rightarrow NO_3^-$
■ Nitrification	$NH_4^+ + 2\,O_2 \rightarrow NO_3^- + H_2O + 2\,H^+$
■ Denitrification	$2\,NO_3^- + 10\,e^- + 12\,H^+ \rightarrow N_2 + 6\,H_2O$
■ Anammox	$NO_2^- + NH_4^+ \rightarrow N_2 + 2\,H_2O$

The main and most abundant source of nitrogen is the atmosphere, where it is found in molecular form (N_2). In this form, it is generally not available to plants, which limits primary productivity in most ecosystems [25]. Only a small group of highly specialized prokaryotes are capable of using nitrogen from the atmosphere, taking N_2 from the air and reducing it to ammonium (NH_4^+), a nitrogenous form that can be uptaken by plants. This process is known as biological nitrogen fixation. While certain nitrogen-fixing organisms are free-living, others need to form symbiotic associations with a host to complete the process. [26]. Among the latter, the rhizobial and actinorhizal symbiotic systems stand out for their high efficiency [27]. All nitrogen-fixing organisms are characterised by the nitrogenase enzyme complex, which is responsible for the reduction reaction of N_2 to NH_3/NH_4^+. In this way, the soil is enriched in nitrogenous compounds that can be assimilated by the plants that serve as food for herbivores, and through them for carnivores, thus incorporating nitrogen into their organism. Later, through excretion and the decomposition of plant and animal residues, nitrogen returns to the soil, this time in the form of ammonium (NH_4^+); this process is named mineralization. This NH_4^+ remains in the soil to be absorbed by plants that do not have the nitrogenase system [28].

During nitrification process, a series of aerobic nitrifying bacteria transform the NH_3/NH_4^+ produced during mineralization initially into nitrite (NO_2^-), and finally, it is oxidized to nitrate (NO_3^-), the nitrogenous form primarily assimilated by the radicular system of plants. The nitrification process is particularly important as it produces an extra supply of nitrogen available to plants. Finally, NO_3^- is transformed by denitrifying bacteria into gaseous nitrogen (N_2), which returns to the atmosphere, completing the cycle [29].

The anammox (anaerobic ammonium oxidation) process, also makes a significant contribution to the nitrogen cycle, turning over NO_2^- and NH_4^+ to N_2 gas. This conversion is performed by bacteria of the phylum Planctomycetes, which are present in anoxic freshwater and marine environments [30].

Nitrogen and its cycle are the key for different forms of life as its multiple oxidation states confer to nitrogen a significant biological relevance in the context of microbial metabolism [31].

3. Processes Responsible for Nitrate Pollution in Water

Nitrogen is an essential macronutrient that enables plants and crops to grow, but excessive concentrations in water are detrimental to people and nature. The nitrate ion (NO_3^-) is the most thermodynamically stable nitrogenous compound present in aqueous and oxygenated earth systems, so there is a tendency for all nitrogenous materials to be readily converted to nitrate in these environments. The release of massive levels of nitrate ions into waterbodies causes cumulative impacts on living organisms and ecosystems. Nitrate pollution is widespread throughout the world in recent decades because of anthropogenic actions and natural processes, and a number of studies have been recently published warning of its consequences [31–34].

The processes responsible for the accumulation of nitrates in different ecosystems are many and varied, and it is recognized that they can be divided broadly according to their origin as geogenic or anthropogenic processes, depending on whether the source is natural or directly related to human action [34,35].

Geogenic sources of nitrogen compounds in the environment include weathering and erosion of igneous rocks and minerals [36], lightning storms through different precipitation and rainfall modes [37], and atmospheric deposition of nitrogen oxides and symbiotic fixation by selected plants and cyanobacteria [38]. All these processes are responsible for the input of nitrogenous forms into the soil, which enter the biogeochemical cycle, and under normally oxidizing conditions lead to their accumulation in the form of NO_3^-, which are easily leached to deep layers and reach groundwater bodies.

Runoff processes that displace large quantities of soil, due to torrential rainfall, are increasingly frequent in certain areas of the planet and also entail the entrainment and incorporation of significant levels of NO_3^- and other nutrients into waterbodies.

The main environmental contamination with NO_3^- has typically been attributed to anthropogenic activities. Due to anthropogenic actions, the natural nitrogen (N) cycle has been significantly altered by a 100% increase in the rate of N influx into the global N cycle. The abuse of organic and inorganic N-based fertilizers in agriculture is a major source of diffuse pollution, contributing to the increase of NO_3^- contamination in waterbodies and to the increase of nitrous oxide in the atmosphere [39,40]. Nitrogen is one of the three macronutrients for plants (N–P–K), and its application has a direct influence on the development of plants, which is why it tends to be abused to ensure maximum agricultural yields. Intensive agricultural practices also lead to a high demand for nitrogen fertilizers. Inorganic nitrogen is normally added to the soil as NH_4^+ and NO_3^- in quantities above the nutritional needs of plants, and is therefore not partially assimilated by crops and leaches from agricultural irrigation and rainfall to be discharged into surrounding waterbodies [41]. Although there is a direct correlation between the higher consumption of nitrogen fertilizers and the increase in crop production to supply the world's growing population, concerns have been expressed about the environmental sustainability of these activities in terms of the impairment they cause to water resources [40].

Intensive livestock production, and the proliferation of large-scale farms, is also a potential source of NO_3^- pollution. Livestock waste contains nitrogen in the form of both organic and inorganic compounds. Microbial action breaks down waste containing organic nitrogen into NH_4^+, which is then transformed into NO_2^- and NO_3^- [42]. NO_2^- is further readily converted to NO_3^-. Thus, organic waste generated from livestock farming is a potent source of NO_3^- inputs that pollute surrounding waterbodies.

Population growth and the development of densely populated urban centres are also responsible for the increase of NO_3^- in wastewater. Urban runoff also pollutes surface waters in many parts of the world. In some scenarios, urban landfills and poorly insulated septic tanks are also involved in nitrate seepage and contamination [34].

Different industrial processes also contribute to NO_3^- pollution in the environment. Chemical industries using nitrogenous commodities (ammonia, nitric acid, urea, and ammonium nitrate) may cause nitrate contamination problems [37]. In these plants, the inappropriate handling and waste-mismanagement may also contribute to the leaching of nitrates into aquifer systems. Nitrate is often present in waters associated with mining because of ammonium nitrate-blasting activities [43].

Deforestation and forest fires also lead to a deterioration of the soil structure and a decrease in its capacity to retain and assimilate NO_3^-, which will therefore be easily washed into deep layers and migrate to the groundwater.

4. Nitrate Removal Technologies in Waterbodies

With the growing international concern about the problem of rising nitrates and their impact both to the environment and to human health, the issue remains: what technical solutions are currently available to control nitrate levels in waterbodies? There are several possible technologies for nitrate removal, some classic and some more innovative, but none is fully deployed and none clearly stands out from the rest [33].

Denitrification of waterbodies to ensure safe nitrate levels can be performed through either separation-based or transformation-based technologies [20,44]. Separation techniques remove nitrate from the water stream to be treated, concentrating them in a second waste product, known as brine, that would have to be treated or stored in a tank. Transformation-based techniques convert nitrate into other harmless chemical compounds via biological or catalytic pathways (Figure 2).

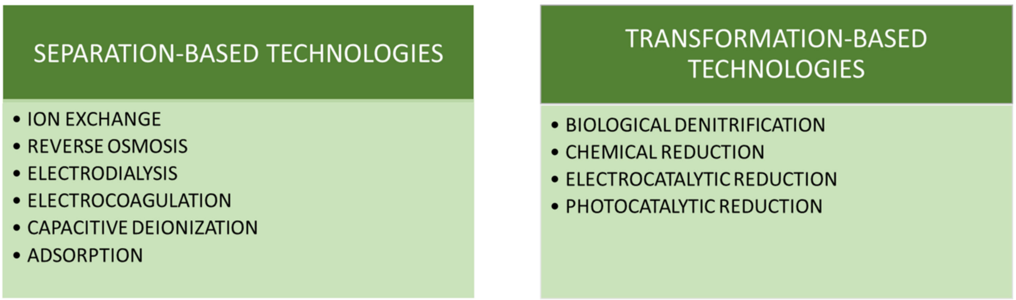


Figure 2. Main technologies for nitrate removal in waterbodies.

4.1. Separation-Based Technologies

Separation methods for the treatment of natural waters contaminated by nitrate (ion exchange, reverse osmosis, adsorption, electrodialysis, electrocoagulation and capacitive deionization) have a long history, and some of them are currently the most widely used. Although, depending on the initial concentration, these techniques provide excellent results, some of them are expensive due to energy costs and do not completely solve the problem, as they do not transform the nitrate into a harmless compound, but generate a concentrated brine, without any economic value and which must be treated or stored appropriately.

4.1.1. Ion Exchange

The ion exchange technology for nitrate removal is efficient and simple, with a low running cost of operation [45]. Anionic resins charged with chloride ions are used, which are exchanged with the nitrate ions present in the water. These systems basically consist of closed pressure vessels containing the synthetic resin. Physically, ion exchange resins take the form of very small beads (resin beads), insoluble in water, acids, and bases, with an average diameter of about 0.5 millimetres. As water is passed through the resin, NO_3^- and other anions are exchanged with Cl^- in the resin, thus increasing chloride concentration into the water.

The typical anion exchange resins generally have sequential anion selectivity of sulphate > nitrate > chloride > bicarbonate [46]. This is a drawback in waterbodies with high sulphate levels as the effectiveness against nitrates is reduced by the presence of sulphate. Besides conventional anion exchange resins, there are also nitrate ion selective resins such as Indion NSSR [47], Purolite A520E [48] or Amberlite IRA 958-Cl [49]. These resins allow satisfactory operation without being limited by other anions that may decrease their efficiency.

Magnetic anion exchange resins with iron oxide particles in the polymeric matrix have also been tested for nitrate removal. Magnetic resin MD218 exhibited high retention capacity and increased selectivity for NO_3^- in the presence of dissolved organic matter, while magnetic resin MD217 was highly effective in waterbodies with high SO_4^{2-} levels. Both resins were prepared on the polymer polyglycidylmethacrylate (PGMA) added with γ-Fe_2O_3 [50,51].

After continuous use, the resins become saturated, but they are regenerable and can be reused multiple times. The ion exchange approach is suitable for automatic control, and is not temperature sensitive in the normal operational range. The main drawback of ion exchange is the treatment of the brine solution resulting from the regeneration of the resins. Proper management of this waste must be performed in a sustainable manner to avoid any further environmental problem [43].

4.1.2. Reverse Osmosis

Reverse osmosis (RO) is a membrane-based technology that is used to remove a large majority of pollutants from water by pushing the water under pressure through a semipermeable membrane. The membrane, with a pore size in the range of 0.1 and 1.0 nm, only allows movement of water molecules to pass through, but rejects movement of solute particles across it. This technology can be used to eliminate multiple inorganic and organic pollutants of waterbodies [37,45]. Reverse osmosis is the most widely used technique in water desalination processes for both drinking water and water for agricultural irrigation [52,53].

This separation technique yields a premium quality water in which only a reduced number of volatile organic constituents remain. Nevertheless, RO has a relatively high energy demand, around 1.8–2.0 kWh/m^3 [54], because it requires a high pressure (>6 bar) to pass the polluted water through the semipermeable membrane. In addition, reverse osmosis generates a significant waste concentrate stream (reject brine), containing high concentration of nitrate, as well as other ions [55]. The reject flow stream can be up to 30% of the total treated water flow. This high rejection represents a serious problem in areas where water availability is scarce [20].

The removal rate of contaminants by reverse osmosis depends on the material used for the membrane, pore size, applied pressure, and quality of the feed water. Under optimal working conditions, approximately 85 to 95% of the nitrate ions in waterbodies can be removed with reverse osmosis [56].

The materials used to fabricate reverse osmosis membranes are of polymeric structure, differing in thickness and pore size. The typical polymeric materials used are cellulose acetate and polyamide [57]. In recent decades, significant progress has been achieved in membrane and module manufacturing, such as the development of thin-film composite polyamide membranes with high chemical compatibility, mechanically very resistant, and excellent stability over a wide pH range [58].

To enhance the performance of the final process, nanofiltration (NF) and reverse osmosis (RO) can be coupled for nitrate removal in water with elevated salinity. The NF removes Na^+ and Cl^- ions from the water over $NO_3{}^-$, and the RO mostly eliminates $NO_3{}^-$ ions from the nitrate-enriched NF permeate. This scheme can achieve a reduction of 91–94% of the total $NO_3{}^-$ level in waterbodies [55]. Moreover, these hybrid NF/RO process minimizes the brine reject fraction, making it more sustainable and friendly to the environment [59].

Among the drawbacks to be considered in membrane-based separation processes is fouling, caused by the deposition of foreign matter from the feed water on the active surface of the membrane, due to their contact with soluble matter, organic matter either as colloidal or suspended particles, resulting in decreased permeation flux and salt rejection [60,61]. In the case of fouling by salt deposits, the phenomenon is known as inorganic scaling. The salts causing the most important inorganic fouling problems in reverse osmosis are calcium sulphate and calcium carbonate [62]. These concerns can be minimized with proper pre-treatment of the feed water, which will result in longer membrane life and lower operating costs.

4.1.3. Electrodialysis

Electrodialysis (ED) is a widely recognised membrane-based technology for nitrate removal, similar to reverse osmosis, except that in this case, ions are transferred through a semi-permeable ion exchange membrane from a more concentrated solution to a less concentrated solution by providing an electric field [63,64]. This is an electrically driven process. This technology has proven to be reliable, exhibits excellent accuracy, and is easy to operate [65].

This separation process is carried out in a filter-press equipment consisting of thin chambers between a pair of electrodes that generate an electric potential difference that enables the movement of the ions (Figure 3). These chambers are formed using intercalated cation and anion exchange membranes; the former allow the passage to cations and the latter to anions. In this way, the electric flow causes some chambers to run out of ions (diluate) and other chambers to have an increasing number of ions (concentrate). The sequential unit of a conventional cellstack (cell pair), consists of an anion exchange membrane, a diluate, a cation exchange membrane, and a concentrate [66,67].

The effectiveness of nitrate exclusion is significantly affected by the cell voltage, which is a key factor in nitrate removal by ED, since it is the driving force for separation across the membranes [68]. When the membrane potential was upgraded from 10 V to 30 V, the nitrate concentration in the diluate stream gradually decreased (31% and 71%, respectively) in 240 min with CMX-AMX NEOSEPTA ion exchange membranes. As the membrane potential increases, more ions can be transported across the membrane, as the movement of ions is enhanced by the increased conductivity generated by the higher voltage [34]. The maximum current efficiency was attained at 20 V [69].

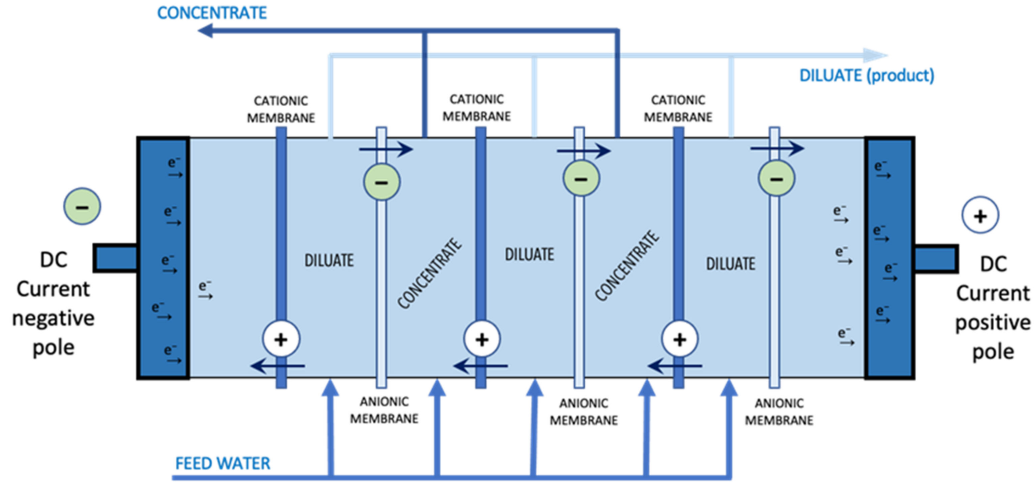


Figure 3. Schematic view of the electrodialysis (ED) process.

The initial nitrate concentration is a parameter that also determines the efficiency of the ED process as the mobility of these ions is facilitated by increasing the ionic strength of the solution [65]. Temperature is another factor that affects the efficiency of the ED process. It has been reported that running at a steady voltage of 15 V, the nitrate exclusion effectiveness goes from 73% to 76.6% and 82.6% depending on whether operating at 15 °C, 25 °C, or 40 °C [70]. The positive impact of temperature on the processing efficiency is related to the fact that temperature reduces the viscosity of the solution, increases the velocity of the ions, while promoting membrane dilatation, which in general improves the permeation of ions through the membrane [66]. In the ED process, the balance of ions between the charged sites on the membrane surfaces is controlled by the pH of the solution. For nitrate removal, weak acidic media greatly enhance electrodialysis due to the no competition between NO_3^- ions and H^+. In contrast, under alkaline conditions, OH^- ions significantly block the NO_3^- movement, thereby reducing nitrate removal [71].

Electrodialysis is a technology that combines the advantages of selectivity and low chemical demand to remove nitrate ions from waterbodies. It is also worth noting that ED requires significantly lower operating pressure than reverse osmosis, its membranes are longer-lived, and the plant size can be adapted easily to the user's needs [43]. There are some disadvantages such as the fact that, in some situations, a pre-treatment stage of the feed water may be necessary depending on the level and type of pollutants it contains. Moreover, the water obtained after the electrodialysis process may require pH regulation and the concentrate obtained from membrane washing may need specific disposal [51].

4.1.4. Electrocoagulation

Electrocoagulation (EC) is an innovative technology in water treatment to remove pollutants. It is an electrochemical process that removes suspended, emulsified, or dissolved pollutants from water using electric current [72]. The goal of EC is that contaminants present in the water form aggregates, producing solid particles that are less colloidal and less emulsified (or soluble) than those in the equilibrium state. When this occurs, the contaminants form hydrophobic components that precipitate and/or float and can be easily removed by some secondary type of separation method. The coagulant is released by electrolytic dissolution of a sacrificial electrode (anode). The dissolution of this anode generates a gaseous flow (O_2, H_2) that aids the flotation of the aggregates. Sometimes, it may be necessary to add a (supporting) flocculant to enhance flotation performance [73].

Key factors influencing EC performance are the electrode metal (usually Fe or Al), current density applied, electric charge per unit volume, and pH of the solution. Commercial EC systems are typically powered at a steady current (5–20 mA/cm^2) to achieve an efficient result [74].

The most critical aspect of the EC process is the coagulant–pollutant interaction. After the coagulant metal is solubilized in water, it undergoes various hydrolysis processes, generating different hydroxometallic compounds, some of which eventually polymerise, as well as precipitating metal hydroxides. [75]. The species and quantities formed (speciation) mostly are dependent on pH and metal concentration [76]. The coagulant substances occurring in the cell will determine the coagulation/destabilization mechanisms and the performance of the overall removal process [77]. Nitrate ions can be effectively removed from waterbodies through adsorption on the particles of metal hydroxides produced from Fe or Al electrodes [75,78].

The strengths of the EC for water pollutant removal are its wide applicability, easy scaling, minimal chemical dosing requirements, reduced sludge production, operation at atmospheric pressure and ambient temperature, simple equipment, and low-medium capital investment costs [74,79]. Moreover, the versatility of adjusting the applied intensity to improve treatment intensity simplifies process control and automation [80]. The weaknesses of this technology lie in the anode passivation through time and sludge deposits on the electrodes, which negatively affect the electrolytic process when operating continuously Furthermore, sacrificial anodes are consumed and need to be renewed regularly [81].

4.1.5. Capacitive Deionization

Capacitive deionization (CDI) is another emerging technology for the removal of ionic pollutants from waterbodies [82,83]. The basis of the CDI process is the removal of dissolved ions by the application of a constant potential between two porous electrodes immersed in water. By polarizing the electrodes, one positively and the other negatively, the ions move from the solution to the electrode surface: the cations migrate to the cathode and the anions to the anode [84]. The salt ions are electrosorbed by pore filling the surface of the electrodes and afterwards released into a concentrated brine solution by shorting the system or switching the voltage. Therefore, it can be stated that by means of CDI, deionization is carried out and simultaneously, energy storage is produced. This fact is one of the key aspects of capacitive deionization since it allows recovering part of the stored energy as a supercapacitor by means of a discharge stage, also called regeneration [85]. The name regeneration refers to the fact that the electrodes, by means of discharge, desorb the ions, leaving them in a state equivalent to the initial state, without ions electrochemically adsorbed on their surface. In CDI, low voltage (<1.5 V) must be applied to avoid water hydrolysis and Faradaic reactions, causing a decrease in energy efficiency, desalination yield, and electrode lifespan [83]. In terms of energy requirement, CDI may compete cost-effectively with membrane-based technologies when operating with water streams of medium or low concentrations. [84].

The nitrate ion is characterised by its planar configuration with a tendency to solvate with H_2O molecules [86], which facilitates its inclusion in the slit-shaped micropores [87,88] present in carbonaceous electrodes used in CDI. Thus, CDI eliminates more than 90% of the nitrate ions from brackish groundwaters in only 15 min. [89]. To enhance the processing efficiency, the electrodes used in CDI can be activated by using phosphoric acid solutions that increase the number of mesopores and hence their specific surface area [90]. To improve their selectivity for nitrate ions, the electrodes can also be treated with surfactants such as cetyl-trimethyl-ammonium bromide, or anion exchange resins [20,91].

Conventional CDI with carbonaceous electrodes tends to have a significantly lower energy efficiency than expected due to co-ion expulsion [92]. This phenomenon occurs when ions of the same polarity as that of the electrode interfere by being adsorbed and desorbed from the pores continuously, which thereby reduces the number of counterions that may be eliminated from the water stream [82]. To ameliorate these issues, membrane capacitive deionization (MCDI), as a derivation of the original CDI, has been receiving increasing attention in recent years. In MCDI, a cation exchange membrane is arranged over the cathode, and an anion exchange membrane over the anode, which serves to inhibit the respective transport of anions and cations. This is to reduce the cited co-ions effects and enhance the salt removal rate, as well as to provide a protection barrier to prevent adverse redox reactions on the electrode surface [93]. The MCDI treatment of contaminated groundwater was able to reduce nitrate levels from 233 mg/L to 4.7 mg/L with a low potential (0.86 V) and reduced energy demand (0.4 kWh/m^3) [94].

A novel approach referred to as catalytic capacitive deionization (CCDI), which combines targeted heterogeneous catalysis with CDI to substantially minimize residual waste products, has recently been announced [95]. In CCDI, porous electrodes containing catalytic In and Pd nanoparticles are used to achieve electrostatic adsorption of nitrate anions and transform them into innocuous N_2. This CCDI equipment, working at a potential of 1.5 V, eliminated 92% of the nitrate present in the feed water, with a successful selectivity of 91% to N_2 of the adsorbed nitrate. [95].

Capacitive deionization is an energetically efficient and commercially viable technology for the desalination of water with moderate salt content [96]. The main limitations of CDI applied to nitrate removal are that the electrodes must be periodically regenerated, and the low selectivity of the electrodes towards nitrate ions, which means that in the presence of ions of similar characteristics (size and charge), interferences will occur and the performance of the process will be lower. On the other hand, it is a novel technology whose equipment has a relatively high market price [84]. Innovative approaches of this technology (MCDI, CCDI) are able to increase its efficiency in specific situations.

4.1.6. Adsorption

Adsorption refers to mass transfer surface processes in which a substance (adsorbate) from a fluid phase becomes incorporated onto a solid phase (adsorbent). The adsorption process has been widely considered for pollutant removal in waterbodies as a consequence of its technical feasibility, simple operation, affordable costs, and the possibility of using multiple adsorbents of the most diverse nature [4,43,97].

An adsorbent must stand out for its surface area, together with its porosity (pore size and volume). Particle size also affects sorption capacity, but in porous materials, this impact is minor compared to the enhanced retention observed with an increase in specific surface area and/or a reduction in pore size [98]. The presence of easily ionizable groups on the sorbent surface will also enhance its adsorptive capacity [99].

The chemical and physical characteristics of the adsorbate (molecular size, polarity, composition, and solubility) also determine whether it is strongly or weakly retained. The specific features of nitrate ions such as their negative charge, ionic size (179 pm), charge density, and the presence of unpaired electrons on the oxygen atoms are key factors influencing the availability to be retained by a given adsorbent [100]. Ionic strength, temperature, and pH of the medium are also crucial parameters of the adsorption process [97].

The adsorption approach has been tested for the remediation of nitrate-polluted waterbodies with a wide range of adsorbents, including granular activated carbon [101], zeolites [102], sepiolite [103], layered double hydroxides [104], pumice [105], chitosan [106], fly ash [107], and other biosorbents and biochars [108,109]. In application of the guidelines for a circular economy, strategies for the recovery of biomass from agrifood and industrial wastes are multiplying in terms of sustainable technological management and green approaches [110]. In this field, there are many studies that propose to transform these wastes into valuable sorbent material to be used in the bio-removal of nitrate ions in waterbodies [111–115].

Nanomaterials have recently gained a reputation as an excellent alternative to conventional sorbents for nitrate removal because, due to their extremely small size, they have a large specific surface area and, therefore, a higher sorption capacity [116,117].

Conventional adsorbents, in general, do not have an elevated uptake capacity, but they can be subjected to surface modifications or activations, both physical and chemical, to significantly increase their removal efficiency [4]. These activation processes will depend on the nature of the adsorbate, and in the case of nitrate ions, the following have been described as the most effective: protonation [118], grafting of amine groups [119], impregnation with metals or metal oxides [120], or the incorporation of cationic surfactants [121] (Figure 4).

The simple heat treatment of the sorbent has also been found to achieve, in some situations, a significant activation of its nitrate retention capacity, especially in the case of layered double hydroxides [104].

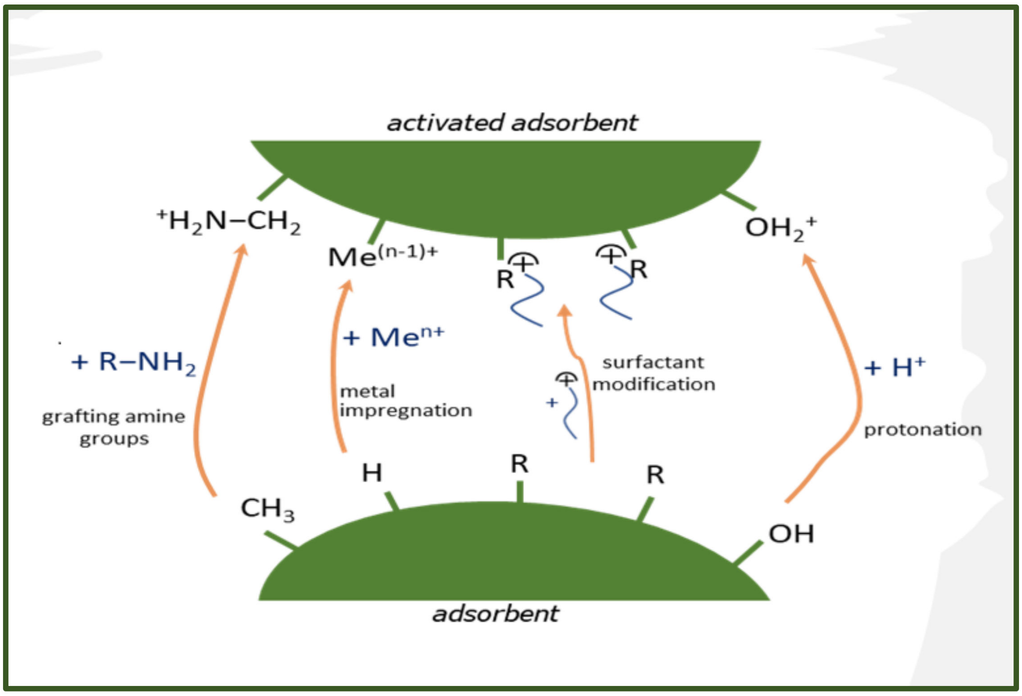


Figure 4. Schematic illustration of surface functionalization of sorbents.

The mechanism of nitrate adsorption will be dependent on the structure, chemical composition, and surface properties of adsorbents and adsorption conditions. Thus, depending on the situation, NO_3^- may be fixed to the sorbent by electrostatic interactions, complexation, ion exchange, and/or hydrogen bonding [65,122].

Other anions present in the water that tend to bind to the reactive surface of the adsorbent will reduce its nitrate retention efficiency. Thus, it is reported that, in selected sorbents, the competing anions (mainly PO_4^{3-}, SO_4^{2-}, HCO_3^- and F^-) significantly affect the nitrate uptake performance [123,124].

A variety of adsorbents of very diverse origin have been reported to remove nitrate ions from waterbodies. Figure 5 displays the sorption capacity values of selected adsorbents. The data shown are all from adsorbents activated by one of the methods already referred to, since due to the specific nature of nitrate ions, raw adsorbents do not show remarkable adsorption capacity. Disparity in values is observed, ranging from more than 225 mg/g (amine functionalized cellulose) to as low as 3 mg/g (polydopamine modified zeolite).

Regeneration and recycling of charged adsorbents are essential for an eco-friendly operation and for minimizing the need for adsorbents, especially when they have required a time-consuming and reagent-intensive activation process. The energy required in this operation must also be taken into account. To this end, desorption and recovery of adsorbents in adsorption–desorption cycles could help to circularize the process and achieve waste reduction. The use of recovered nitrates is not a problem, since they can be added to agricultural lands as a nitrogen fertilizer [123].

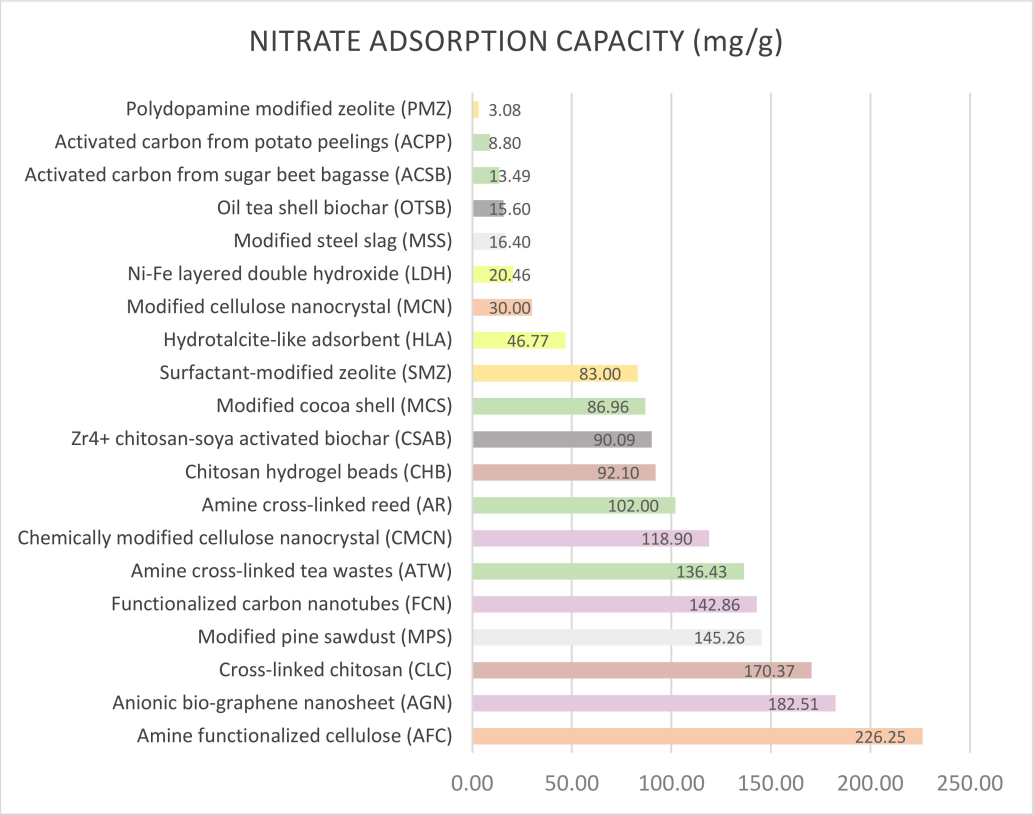


Figure 5. Nitrate adsorption capacities of selected sorbents. PMZ [125], ACPP [126], ACSB [113], OTSB [127], MSS [128], LDH [129], MCN [130], HLA [131], SMZ [121], MCS [118], CSAB [100], CHB [132], AR [133], CMCN [130], ATW [134], FCN [135], MPS [136], CLC [106], AGN [137], AFC [138].

4.2. Transformation-Based Technologies

These technologies, applying different procedures depending on the specific process, are to convert nitrates normally into N_2 gas, to be released into the atmosphere without side effects. Technically, it is a reduction process that can be performed by microorganisms or by chemical, electrochemical, or photochemical reactions.

4.2.1. Biological Denitrification

Biological denitrification is a metabolic process by which bacteria, mainly under anaerobic conditions, biodegrade organic matter and use nitrate as terminal electron acceptor, leading finally to the inert gas N_2 [139].

Three groups of denitrifying bacteria are distinguished depending on which substances they use as an energy source: autotrophic bacteria (oxidise inorganic compounds), heterotrophic bacteria (oxidise organic compounds), or mixotrophic bacteria (oxidise both inorganic and organic compounds). Autotrophic denitrifying bacteria use H_2 gas or reduced sulphur compounds as the energy source (electron donors) and an inorganic carbon source, usually CO_2 or bicarbonate [20,140]. Most biological denitrification treatments are based on heterotrophic bacteria that need a source of organic carbon, such as methanol, ethanol, or acetic acid [141,142], but methods have also been developed in which a gaseous substrate as CO or CH_4 is used [143].

Heterotrophic biological water denitrification treatments have been applied on an industrial scale to a greater extent, mainly due to the faster rate at which this process is carried out. In the case of autotrophic denitrification, longer spatial times are required [144], which leads to bigger reaction volumes and considerably increased costs.

Typically, during the process of biological denitrification, pre-treatment of the water is required, in which the nutrient carbon source and electron donor substances are incorporated. Post-treatments are also performed at the outlet of the bioreactor to adjust water quality to its final use (Figure 6).

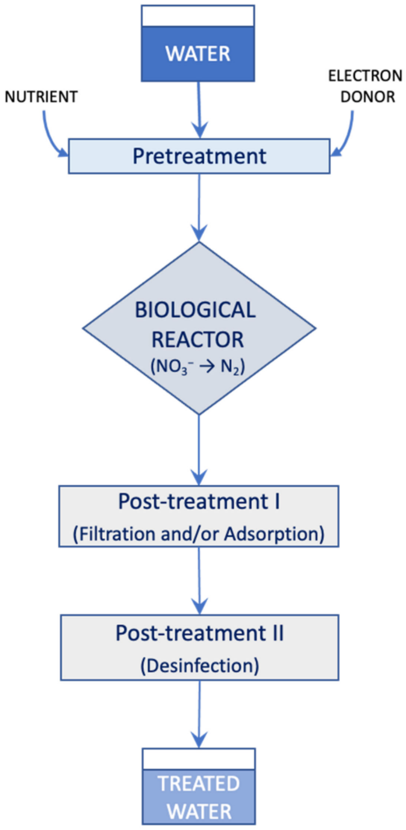


Figure 6. Flowchart representing a typical biological denitrification process (adapted from [142]).

Autotrophic denitrification is performed by bacteria as *Thiobacillus denitrificans*, *Thiomicrospira denitrificans*, *Azoarcus denitrificans*, or *Bosea thiooxidans* [145,146]. These microorganisms are mainly mesophiles with an optimum temperature between 25 and 35 °C. In this process, alkaline substances are added (HCO_3^-, $CaCO_3$) to neutralize the H^+ produced [147]. These bacteria also have the ability to use O_2 as electron scavenger for the oxidation of sulphur compounds. The final product obtained will depend on the oxygen concentration. At low O_2 concentrations (<0.1 mg O_2/L), partial oxidation to S^0 occurs, while at high O_2 concentrations, SO_4^{2-} is produced [142]. To enhance nitrate removal, the presence of oxygen should be avoided since the bacteria will preferentially use oxygen as an electron acceptor.

Under autotrophic conditions, it is critical that the proportion of nitrate ions and sulphur compounds is balanced in a stoichiometric ratio so that the reducing bacteria can operate properly [148]. When raw water contains high concentrations of nitrate, an effluent with high sulphate content is obtained. In this scenario, the generation of anaerobic zones could result in the formation of sulphides [149].

Heterotrophic denitrification processes that occur under anoxic conditions are the most investigated and most widely implemented. Recent research has mainly addressed the screening of microbes with high nitrate removal efficiency [150]. So far, a large number of heterotrophic bacteria, such as *Alcaligenes* sp., *Pseudomonas* sp., *Paracoccus* sp., *Acinetobacter* sp. and *Bacillus* sp., have been reported [146,151,152].

Nitrate reduction proceeds stepwise in accordance to:

$$NO_3^- \text{ (aq)} \rightarrow NO_2^- \text{ (aq)} \rightarrow NO \text{ (g)} \rightarrow \frac{1}{2} N_2O \text{ (g)} \rightarrow \frac{1}{2} N_2 \text{ (g)} \quad (1)$$

Each stage is catalysed by an enzyme complex, the synthesis of which will occur under partially aerobic or anaerobic conditions [153]. The first step of denitrification is the reduction of NO_3^- to NO_2^-, catalysed by nitrate reductase. The second step is the transformation of NO_2^- to nitric oxide (NO) by nitrite reductase. The reduction of NO to N_2O is catalysed by nitric oxide reductase. Among the denitrification enzymes, this is the least characterized. The last stage of denitrification is the reduction of N_2O to inert N_2. It is carried out by the enzyme nitrous oxide reductase [154]. This enzyme is severely limited by the presence of O_2. Because of this, it is important to avoid the entry of oxygen into the denitrifying process, so as not to release N_2O, a gas that contributes to the global greenhouse effect. Some evidence revealed that the presence of Cu^{2+} in the raw water of a continuous denitrifying reactor is important in preventing the accumulation of N_2O during the removal of high nitrate concentrations [155].

As a staged process, there is also the possibility of accumulation of intermediates (NO_2^-, N_2O, NO) depending on the characteristics of the feed water and the organic substrate used. Moreover, the operating conditions (temperature, pH, hydraulic retention time, and cell retention time) will be critical. Based on this, for the transformation to culminate in N_2, environmental conditions such as dissolved O_2 level, organic carbon source, nitrate concentration, C/N ratio, phosphorus availability, pH, temperature, and the possible presence of toxics must be controlled [156].

Groundwater has a low content of dissolved organic compounds. Therefore, it is necessary to add external carbon-containing substrates to facilitate nitrate removal by biological denitrification [157]. Liquid state electron donors (methanol, ethanol, sucrose, acetic acid, glucose syrup, starch, and molasses), as exogenous carbon source, have been successfully applied in different heterotrophic denitrification processes, showing an excellent efficiency [158]. Solid organic carbon donors as cellulose-based products (woodchip) [159] and different biodegradable polymers [160] are also commonly used.

Numerous biological denitrification processes have been reported; in general, the results obtained are quite good, although they are affected by the specific conditions of each case. Denitrification efficiencies of 95–100% are reported using ethanol as an electron donor in waterbodies with elevated (>250 mg/L) nitrate concentration [161,162]. Autotrophic denitrification is also generally considered to be cost-effective, scalable, targeted and highly efficient in a variety of situations. Using H_2, S^0 or S^{2-} as electron donors, in packed-bed, fluidized-bed or membrane biofilm reactors and with contaminated groundwater or potable water, 98–100% denitrification efficiency was achieved [148,154,163].

Fluidized bed and fixed bed reactors are the preferred types of reactors for this biological treatment, with fluidized bed reactors providing the highest nitrate removal rates. However, with these reaction systems, greater control of the process is required. Although biological denitrification is very effective in nitrate removal, it has some drawbacks, such as a decrease in the denitrification rate as the temperature drops, leading to the need for additional treatment of the water [142,158]. Thus, biological denitrification can lead to microbial contamination of treated water, and regulators require post-treatment using membrane technology as a method of protection. In this context, membrane bioreactors (MBR) offer an integrated approach, with the MBR effluent requiring little additional disinfection, if any. It is remarkable a hollow fibre membrane reactor developed by Zhou and co-workers [164] combined MBR with a Pd nanoparticle catalyst. The efficiency and selectivity of the process were significantly improved compared to the use of biofilms or palladium catalysts alone.

4.2.2. Chemical Nitrate Reduction

Chemical nitrate reduction proceeds through sequential reactions in which NO_3^- is reduced to NO_2^-, which is transformed to NH_4^+, as an undesirable co-product, and to harmful N_2 as the target product. Different metals, in particular Fe and Al, but also Cu, Pd, and Rh, have been applied as catalysts for this chemical nitrate reduction [142]. Compared to biological denitrification, catalytic denitrification exhibits several advantages, such as being more flexible in operation, less space requirements, easy automatic control, no start-up time, and no odour problems [165]. Compared to electrochemical reduction, the main advantage is its low energy requirement, and it is a technology particularly suitable for the purification of waterbodies with low organic matter content [166].

Chemical denitrification of nitrates by means of zero-valent metals has attracted a great deal of interest, with a special focus on zero-valent iron (ZVI) [142,166–168]. Relevant investigations on the use of bimetallic catalysts, using H_2 as reductant agent, are also significant [169–172].

- Removal of nitrate by zero-valent iron (ZVI)

The application of zero-valent metals (mainly iron) for the reduction of nitrates in water presents many practical benefits, such as simple handling, high efficiency, and low cost.

Different reactions occur during the reduction of nitrate by Fe^0. In fact, nitrate can be transformed directly to ammonium:

$$4\,Fe^0 + NO_3^- + 10\,H^+ \rightarrow 4\,Fe^{2+} + NH_4^+ + 3\,H_2O \tag{2}$$

or to nitrite in a first step, with subsequent reduction to N_2 or NH_4^+:

$$Fe^0 + NO_3^- + 2\,H^+ \rightarrow Fe^{2+} + NO_2^- + H_2O \tag{3}$$

$$3\,Fe^0 + NO_2^- + 8\,H^+ \rightarrow 3\,Fe^{2+} + NH_4^+ + 2\,H_2O \tag{4}$$

The reduction agent is Fe^0, although the production of H_2 by corrosion of Fe^0 in acidic media can also contribute to the reduction of nitrate:

$$2\,H^+ + Fe^0 \rightarrow H_2 + Fe^{2+} \tag{5}$$

$$NO_3^- + 4\,H_2 + 2\,H^+ \rightarrow NH_4^+ + 3\,H_2O \tag{6}$$

The reduction directly to N_2 is also possible, with the formation of OH^-, the accumulation of which can be prevented by pH regulation.

$$5\,Fe^0 + 2\,NO_3^- + 6\,H_2O \rightarrow 5\,Fe^{2+} + N_2 + 12\,OH^- \tag{7}$$

$$10\,Fe^0 + 6\,NO_3^- + 3\,H_2O \rightarrow 5\,Fe_2O_3 + 3\,N_2 + 6\,OH^- \tag{8}$$

The reduction of nitrate by Fe^0 leads to pH increase. The neutralisation of the OH^- produced in the reaction will lead to higher yields in the process; hence, pH control is one of the key factors. [173]. For experiments using microscopic iron, it is observed that nitrate removal efficiencies of 100% are only obtained at low pH values [166]. The usual method of pH regulation is the addition of HCl or acetic acid or the bubbling of CO_2. An oxidation product can appear on the surface of Fe particles in aerobic conditions. It can be black (magnetite, Fe_3O_4) or brown (lepidocrocite, FeO(OH)). The presence of lepidocrocite can slow down the nitrate reduction because the transition of electrons is easier in magnetite. [168].

The reduction of nitrates with ZVI can be enhanced through the pre-treatment of Fe particles and with increasing temperatures [174]. Several mechanisms are involved in the nitrate reduction on Fe0, such as diffusion, adsorption, and chemical reduction, the latter being the controlling step of the process [175].

The influence of chloride ions on nitrate reduction by ZVI is controversial, although agreement is found for high concentrations of chloride ions, which negatively affect the reduction process of nitrate on microscopic ZVI [176]. The presence of phosphate ions causes competition with nitrate for active sites of iron, although better affinity of nitrate to iron is observed [176].

The reduction of the particle size of granular Fe^0 (mm) to 1–100 nm, increases its specific surface area and, thus also increases the reaction rates. It is known as nanoscopic

Fe^0 (nZVI) and can be easily synthesized by the reaction of a ferric salt solution with borohydride [177]:

$$4\ Fe^{3+} + 3\ BH_4^- + 9\ H_2O \rightarrow 4\ Fe^0 + 3\ H_2BO_3^- + 12\ H^+ + 6\ H_2 \tag{9}$$

A better performance of nZVI is observed at high pH values, compared to microscopic ZVI. A 100% nitrate removal is reported in experiments without pH regulation at a starting pH of 7, in aerobic or anaerobic conditions [178,179]. In either case, acidic conditions enhance the nitrate reduction process.

In order to improve the performance of nZVI, and minimise its tendency to agglomerate, the incorporation of different encapsulating substances such as carbon-based materials, clays, or resins has been investigated. A nitrate elimination efficiency of 92% is reported with nZVI encapsulated with carbon nitride. In this laboratory experiment, the selectivity to N_2 reached 97%, with a constant performance at pH from 5 to 11 [180]. Also noteworthy is the 100% removal efficiency and N_2 selectivity close to 80%, without pH control, achieved with nZVI supported on NaY zeolite. [181].

The use of nZVI combined with certain support materials provides excellent nitrate removal efficiency and very good selectivity towards N_2. pH control can be a drawback of this treatment due to the need for additional chemicals to regulate the pH, and to restore neutral pH after treatment. The use of some support materials or the application of ultrasound can overcome this problem. A second major drawback is the release of oxidation products (Fe^{2+}) into the treated solution.

In addition of ZVI, other zero-valent metals have been studied over time. Among the alternative metals, particularly noteworthy are the studies with aluminium (ZVA) and magnesium (SVM).

ZVA shows a higher reactivity than ZVI due to the more negative potential of aluminium ($E_{Al}{}^0 = -1.662$ V and $E_{Fe}{}^0 = -0.440$ V), although high pH values are needed to operate what may produce aluminium hydroxide precipitates in treated water according to reactions of Equations (10)–(12) [167]:

$$3\ NO_3^- + 2\ Al^0 + 3\ H_2O \rightarrow 3\ NO_2^- + 2\ Al(OH)_3\ (s) \tag{10}$$

$$NO_2^- + 2\ Al^0 + 5\ H_2O \rightarrow NH_3 + 2\ Al(OH)_3\ (s) + OH^- \tag{11}$$

$$2\ NO_2^- + 2\ Al^0 + 4\ H_2O \rightarrow N_2 + 2\ Al(OH)_3\ (s) + 2\ OH^- \tag{12}$$

The reduction potential ($E_{Mg}{}^0 = -2.363$ V) and reactivity of zero-valent Mg (ZVM) are quite high and its use is most favourable, as Mg^{2+} lacks the precipitation problems of its hydroxides and does not have any environmental risk [167].

- Catalytic reduction of nitrate over bimetallic catalysts with H_2

The use of a coating metal (mainly Cu^0) on the particles of nZVI was tested to improve nitrate removal and N_2 selectivity. In this system, Cu acts as promoter metal, being the catalyst for the reaction with nitrate, while Fe^0 is the reductant source, restoring Cu^{2+} to Cu^0. When adding H_2 to this reaction system, no improvement in nitrate reduction is observed, due to the poor adsorption of H_2 on the surface of Cu. The incorporation of a noble metal (Pt, Pd, Au, or Rh) to this catalyst, in the presence of H_2 as a reducing agent, shows an enhanced effect on the nitrate reduction performance and the selectivity to N_2, as a result of the better fixation of H_2 on the noble metal sites [169,182].

The general structure of bimetallic catalysts (Figure 7) involves two different metals (a transition metal and a noble metal) on a support material that can be either active, with catalytic reducing properties (ZVI), or passive (zeolite, SiO_2, Al_2O_3, activated carbon (AC), carbon nanotubes (CNT), etc.). Considering the noble metal, Pd showed the highest activation capacity for H_2 [183]. The transition metals acting as promoters, with the most efficient performance were In, Cu, and Sn. Investigations analysing three bimetallic catalysts with nano-crystalline beta-zeolite (NBeta) as support material

(Sn-Pd/NBeta, Cu-Pd/NBeta, and In-Pd/NBeta) concluded that all of them showed high reduction efficiency (>95%) and high N_2 selectivity (>80%). The highest reduction rate was observed for Sn-Pd/NBeta, while Cu-Pd/NBeta exhibited the greatest selectivity towards N_2 (92.7%). When Cu and Sn metals were analysed after the reaction, it was observed that Sn showed a higher rejuvenation ability than Cu, with the Sn surface showing a higher affinity to nitrate [169]. In any case, these results are not extensive for all catalysts, due to synergistic effects in the reduction process between promoter metal and support material.

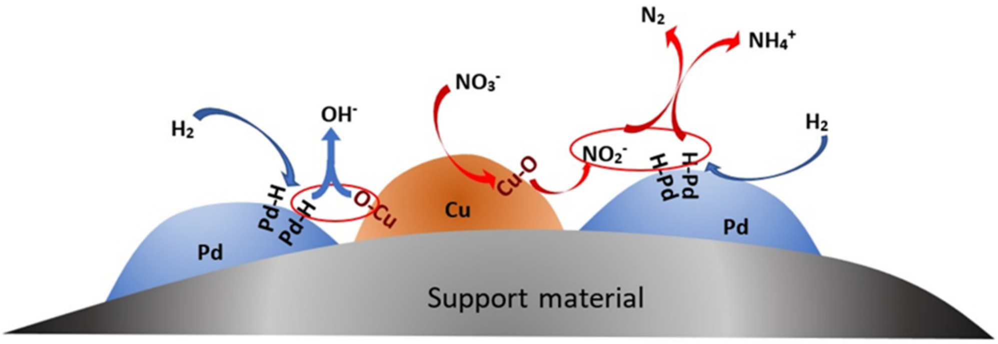


Figure 7. Scheme of the reactions taking place on the surface of a bimetallic catalyst.

Regarding the support material, many researchers have compared the removal performance and N_2 selectivity of different materials [170]. Alumina is the most widely studied support. Other metal oxides studied were TiO_2, ZrO_2 and Nb_2O_5. Carbon-based material, such as AC and CNT, zeolites (NBeta, NZSM-5, NaY), SiO_2, and ZVI-based materials were also investigated [184,185]. The physical properties of these support materials, such as specific surface area, morphology, and porosity, are crucial in the denitrification process. Support materials with higher reactive surface area and porosity, such as γ-Al_2O_3-dyatomita and zeolites, showed high catalytic effect and high selectivity towards N_2 due to a good dispersion of the metal particles on their surfaces. Supports based on ZVI showed high reduction rates, but a high selectivity towards NH_4^+ [183,186,187].

To maximize the process efficiency, several factors need to be taken into account, including: (a) the effect of the loading of the noble and promoter metals; (b) the effect of the loading of catalyst and NO_3^- concentration; (c) the effect of pH and buffer system; and (d) the effect of the H_2 flow rate in the system [185].

The deactivation of the catalyst is one of the main drawbacks of this technology. Factors such as catalyst passivation, leaching of the metal from its support, and aggregation of metal particles after several cycles of treatment affect the life of the catalyst. Results of the leaching test for bimetallic catalysts showed that zeolites and ZVI-based supports are less prone to leaching than metal oxides and carbon-based supports [172]. Moreover, metal leaching was found to have pH dependence.

Most of the research about the catalytic reduction of nitrates was carried out in batch reactors. Experiments in packed beds or trickle-bed reactors present the drawbacks of partial loss of the catalyst, as it is swept away by the flow rate. To overcome this problem, the use of catalytic membrane reactors (CMRs) was implemented. Commercial ceramic membranes, usually alumina nanotubes of a varied porosity, are used to support the bimetallic catalyst. The determinant influence of the membrane pore size on the catalyst performance was verified. Membranes with a smaller pore size (5 nm) achieved up to 92% NO_3^- conversion and 80% N_2 selectivity [188].

The main advantages of chemical nitrate reduction are that no waste stream or brine is generated, as well as the prospect of more sustainable treatment and the multi-pollutant removal potential. As drawbacks, it should be noted that nitrite, ammonium, and nitrogen-containing greenhouse gases are undesirable by-products of nitrate reduction, which must be almost entirely avoided due to their harmfulness. The formation of Fe^{2+} in solution may require some additional treatment step for downstream removal.

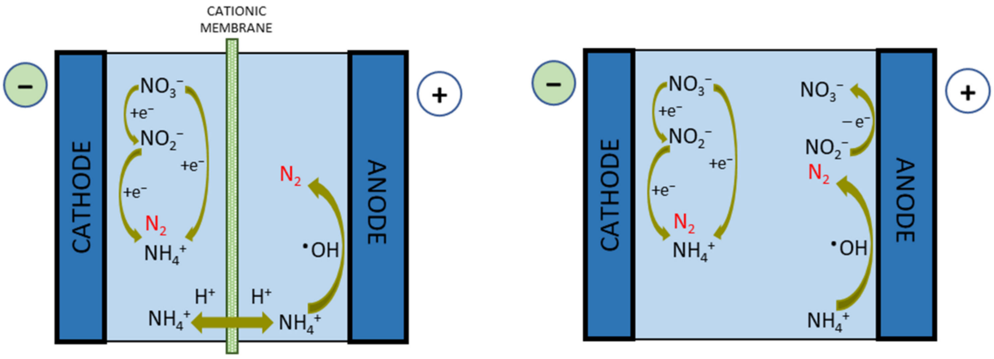
Catalytic processes for nitrate removal are viable technologies but need further research to propose an operating reactor configuration to reduce the above-mentioned inconveniences.

4.2.3. Electrochemical Denitrification

Electrochemically driven technologies for water decontamination are well positioned as efficient solutions because of their great suitability, modular reactor designs, and possibilities to transform pollutants into harmful products [189]. The electrochemical removal of NO_3^- has the advantage of reducing the oxidation number of nitrogen, transforming nitrates into N_2 or NH_3/NH_4^+, as the main products, without the requirement for the addition of chemical compounds. It was shown that reaction products may also contain hydrazine (N_2H_4) and other oxygen-containing nitrogen species (NO_2, NO_2^-, NO, N_2O, and NH_2OH) [190].

The electroreduction of nitrates occurs over the cathode, which is negatively charged (Figure 8). Due to electrostatic forces, nitrates do not touch the cathode surface unless agitation is supplied. It can be accomplished with a static cathode in an externally agitated solution or with a rotating electrode, which achieves turbulent flow conditions at low rotation rates [191]. Depending on the composition of the treated solution, the reduction reaction of nitrates may compete on the cathode with other reduction reactions. According to the potential supplied, hydrogen evolution may occur due to the reduction of the solvent:

$$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^- \tag{13}$$



DUAL-CHAMBER CELL (DCC) SINGLE-CHAMBER CELL (SCC)

Figure 8. Electrochemical reduction of nitrate ions in dual- and single-chamber cells.

At the same time, there are oxidation reactions taking place over the anode, with oxygen evolution being the main one:

$$H_2O \rightarrow \frac{1}{2}\,O_2 + 2\,H^+ + 2\,e^- \tag{14}$$

Due to the presence of other ions, such as chloride, another oxidation reaction may occur:

$$2\,Cl^- \rightarrow Cl_2 + 2\,e^- \tag{15}$$

The generation of chlorine gas is of crucial importance in this process. In fact, the chlorine generated can disproportionate, giving hypochlorite and chloride:

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \tag{16}$$

$$HClO \rightarrow ClO^- + H^+ \tag{17}$$

The presence of hypochlorite in the solution promotes N_2 as the primary end-product of nitrate reduction, due to the breakpoint chlorination reaction:

$$2\ NH_4^+ + 3\ ClO^- \rightarrow N_2 + 3\ H_2O + 2\ H^+ + 3\ Cl^- \tag{18}$$

Although this is not the only product of the reaction between ammonium and hypochlorite, chloramines (mono, di and tri-chloramine) can be produced [192]. These molecules are disinfectants more stable than hypochlorite.

The effect of chloride concentration on the electrochemical nitrate reduction rate is controversial. Szpyrkowicz and co-workers, with Pd-Cu/SS, Pd-Co/Ti, and Pd-Co-Cu/Ti cathodes [193], and Li and co-workers, with Fe, Cu and Ni cathodes [194], reported no improvement or decrease in the nitrates reduction rate with chloride concentration. However, a positive effect of chloride concentration was observed for cathodes such as Zn [195], BDD (boron-doped diamond) [196], and graphite [197]. A positive effect of chloride concentration was also reported using SS (stainless steel) cathode and BDD or DSA anodes in a single chamber cell [192]. In this work, the evolution of chlorine atoms is analysed. It is observed that the BDD anode oxidizes chlorine to its higher oxidation number, giving perchlorate as the final product, specially at low chloride concentrations. With DSA anodes, chlorine is partially oxidized to chlorate. The best performance of these anodes occurs for high chloride concentration (3000 mg/L of NaCl), giving a maximum nitrate reduction rate, excellent selectivity to N_2 gas, and no formation of chlorate or perchlorate [192].

There are many factors that govern the rate of nitrate removal and the products resulting from this reduction in an electrochemical reactor, the main ones being the configuration of the cell, the electrode material, the applied potential, the pH of the solution, and the nature of the supporting electrolyte [198].

Regarding the cell configuration, the electrolytic reduction of nitrates has been studied in a single-chamber cell (SCC) and in a dual-chamber cell (DCC). The distinguishing feature of a DCC is the presence of a cation exchange membrane (CEM) separating the cathodic chamber from the anodic chamber. In DCC configuration, ammonium is the only reduction product able to reach the anodic chamber. In the case of SCC configurations, nitrites can reach the anode and re-oxidate to nitrates, decreasing the cell performance (Figure 8).

When chloride ions are present in solution, its oxidation takes place on the anode (Figure 9). In DCC configuration, the breakpoint chlorination reaction only occurs when ammonium passes across the cation exchange membrane into the anodic compartment [193]. The improvement of DCC configurations has been demonstrated with different cathodic materials (graphite, Cu-Ni, Ti, Pd-Cu/SS, Pd-Co/Ti, and Pd-Co-Cu/Ti) [193,197].

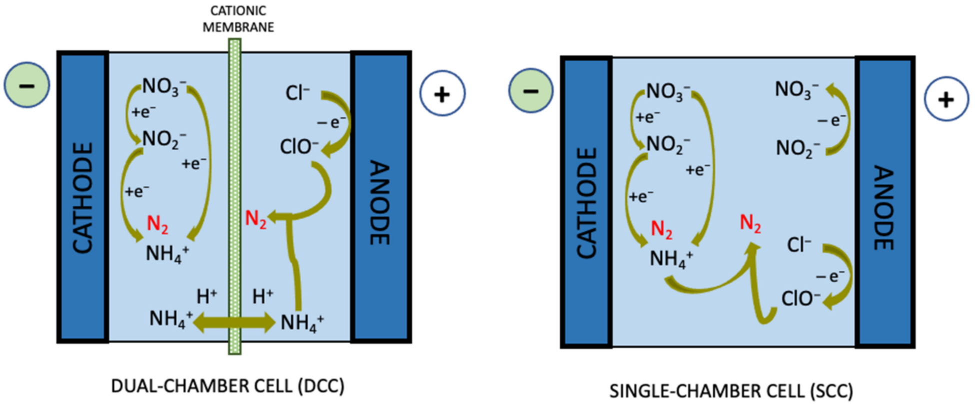


Figure 9. Electrochemical reduction of nitrate ions, in presence de Cl^-, in dual- and single-chamber cells.

In SCC configurations, chloride ions (Cl^-) are oxidized on the anode to hypochlorite (ClO^-), which reach ammonium ions directly in the solution (Figure 9). The presence of chloride ions in SCC configuration increases the selectivity towards N_2 in the reduction of nitrates [192,199,200].

An interesting DCC configuration is the one designed with a Pt anode and Pt-Cu cathode, deposited on both sides of a nafion membrane [201]. In this reactor, O_2 is produced on the anode surface and H^+ flow across the membrane to the cathodic chamber, where they are further converted to H_2 (g), which contributes to the reduction of nitrates.

Regarding electrode materials, different cathode materials have been studied, such as graphite, SS, Ni, Cu, Pt, Pd, Pb, Bi, Sn, Ti, Rh, Fe, BDD, etc. Pd cathodes showed almost no activity in nitrate reduction [202,203], while graphite and Cu electrodes showed the higher activity, yielding nitrite and ammonium as the main products [197,204]. Selectivity towards N_2 was raised up to 100% in the presence of chloride [194]. Significant improvement was obtained using bimetallic cathodes, mainly combinations of Cu with Ni, Rh, Zn, Pd, and Sn. When Cu-Pd electrodes are used, the functional role of Cu is to reduce nitrate into nitrite, while Pd reduces nitrite into N_2 with high selectivity. The cathode combination Cu-Zn performed excellent conversion of nitrates, reaching values of 90% [205] and 94.4% [206], with the suppression of ammonium products when NaCl was added as an electrolyte. With a cathode obtained via the electrodeposition of Cu on a Ni foam matrix, 100% elimination of nitrate was reported, which slightly decreased when NaCl was added to promote the almost complete removal of ammonium [199]. A novel Co_3O_4/Ti cathode was recently tested for nitrate removal with different concentrations of Cl^-. In the absence of chloride, 98% of nitrate removal was reached, with a selectivity of 32% to NH_4^+ in 3 h. On increasing the Cl^- content to 1500 mg/L, the nitrate removal slightly decreased to 96%, but no NH_4^+ was detected as the final product, with almost complete transformation of nitrogen to gaseous species [200].

The pH is also a key factor in the electroreduction rate of NO_3^-, increasing at acidic pH values. At pH > 7.0, hydroxyl species passivate the electrode surface, decreasing the reduction rate [190]. It has been reported an increase of pH from 1 to 7 during the electroreduction process due to the production of OH^- ions in non-buffered solutions. In addition, the final products of the electroreduction process depend on pH, increasing the production of nitrites as pH is elevated [207,208].

4.2.4. Photocatalytic Denitrification

Heterogeneous photocatalysis has received increasing attention in recent years as an interesting alternative to conventionally applied technologies for the treatment of polluted water. In this context, photocatalytic reduction is identified as a suitable technology for the denitrification of waterbodies [209,210]. It was first reported in 1998 by Li and Wasgestian [211]. The process starts with the absorption of radiation of a certain wavelength, which excites a semiconductor that functions as a photocatalyst. Irradiation induces the formation of electrons (e_{CB}^-) in the conduction band and holes (h_{VB}^+) in the valence band (electron-hole pairs) in the semiconductor, which can migrate to its surface, generating highly reactive radicals capable of degrading the pollutants in the medium. The minimum energy to excite an electron from the valence band to the conduction band is known as band gap energy. The incident photon must reach or exceed this energy to generate the (e_{CB}^-)/(h_{VB}^+) pair [210].

The light-driven excited states of the photocatalyst enable the transformation of NO_3^- to N_2 gas. The photoreduction of nitrate ions occurs by reaction with electrons e_{CB}^- or by reaction with $CO_2^{\bullet-}$ radicals generated by the interaction of hole scavengers (formic acid, methanol) with the holes (h_{VB}^+) in the valence band (Figure 10) [212,213]. The photocatalytic activity and selectivity are affected by the nature of the photocatalyst and hole scavengers used in the process [214]. Titanium dioxide (TiO_2) is the classic photocatalyst on account of its reduced cost, excellent stability to chemical corrosion, catalytic activity in the whole pH range, harmless behaviour towards humans, and efficiency to avoid the production of NO_2^- and NH_4^+ as co-products [215]. However, its broad band gap energy (3.2 eV) limits its absorption of solar radiation to the UV light range ($\lambda < 390$ nm), which only represents about 5% of the solar spectrum. This material also shows a high regeneration rate of electron-hole pairs that restricts its photocatalytic activity. Alternative materials are investigated to overcome these drawbacks; essentially, materials that can be activated in the region of the visible range make the best use of the solar spectrum. In this respect, it has been proven that the addition of Ag nanoparticles improved the catalytic activity of TiO_2 to reduce NO_3^-, due to the existence of Ag-TiO_2 junctions on the catalyst surface that increased its photoactivity [214].

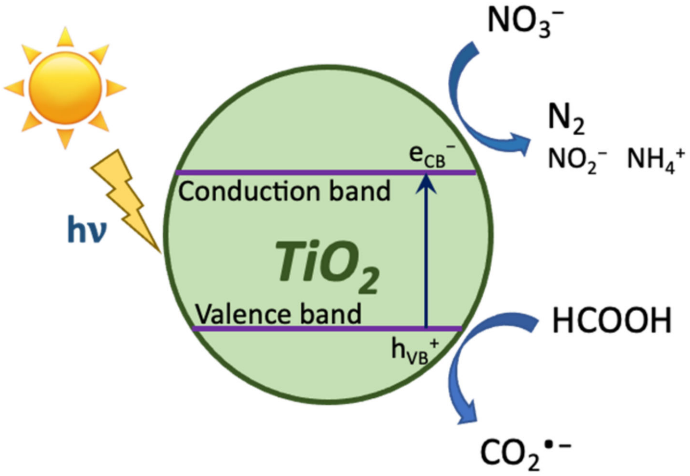


Figure 10. Nitrate photocatalytic reduction on TiO_2.

Both monometallic (Pd, Ag, Cu) and bimetallic (Pd/Ag, Pd/Cu) photocatalysts were investigated for the removal of nitrate under solar irradiation, assessing the effect of different scavengers as reducing agents (acetic acid, formic acid, ammonium oxalate, and oxalic acid) on the efficiency of the denitrification process [216]. To improve the activity of bimetallic catalysts, different support materials such as hydrotalcite, acrylic resins, ZrO_2 or $NaTaO_3$ nanoparticles are incorporated [217]. In recent years, bismuth-based photocatalysts have also exhibited outstanding performance in efficient nitrate reduction via visible-light photochemical reactions [218]. Photocatalytic denitrification frequently leads to the formation of non-desired NO_2^- or NH_4^+ instead of up to N_2, which is linked to intrinsic characteristics of the catalysts, mainly a high valence band potential. Finally, the global yield is affected by electron-hole recombination, as is common in other photocatalytic reactions [213].

The commercial implementation of photocatalytic denitrification is still restricted by the unavailability of a cost-effective, visible-light active catalyst along with a relatively limited comprehension of photoreactor designs.

5. Alternative Strategies

Other alternative technologies to those already mentioned are available and could be implemented for nitrate removal, depending on the specific situation to be addressed. The solutions that have recently received the most attention are those based on natural processes [43].

Phytoremediation is one of the techniques categorized as a nature-based solution, and involves the use of plants and plant-derived microbes to eliminate pollutants from soil and water. Phytoremediation of water is an ecotechnology, based on the ability of some plants to tolerate, absorb, accumulate, and degrade pollutant compounds. Compared to traditional physical–chemical techniques, phytoremediation has several advantages, among which we can highlight its lower economic cost, its more respectful approach to the ecological processes of the aquatic ecosystem, and the fact that it is a more socially, aesthetically, and environmentally accepted technology. It is therefore not surprising that phytoremediation is increasingly seen as an environmentally friendly alternative to physical-chemical technologies. This approach offsets the expensive cost of physico-chemical processes and is an affordable option for economically deprived regions where conventional water treatment plants cannot be financed. Plants, powered by solar energy through photosynthesis, while absorbing nitrates and other pollutants present, also increase dissolved oxygen levels [219].

The phytoremediation process may use several strategies to reduce the pollutant content, such as phytoextraction, phytovolatilisation, phytostabilisation, phytodegradation, rhizodegradation, or rhizofiltration [220]. These strategies to bioremove nitrate from polluted waterbodies are based on the capacity of aquatic plants to absorb nitrate for their growth. With the ultimate aim of restoring the damaged ecosystem, the behaviour of plants such as bamboo, water lilies, cattail, water lettuce, water hyacinths, arrowhead, poplar, and eucalyptus were investigated [43,219,220].

Constructed wetlands (CW) are systems designed to reproduce and optimize the pollutant removal processes in the same way as they occur in natural wetlands and are also an interesting option for the treatment of nitrate-polluted water. CWs are treatment frameworks that use wetland vegetation, soils, and their related microbial gatherings to remediate the contaminated destinations. They are considered a natural, simple, affordable, and green technique for water treatment. The close interplay between growing vegetation, root-associated microbes, and substrate performs a determining influence in the removal of pollutants [43]. CWs offer a preferred alternative for wastewater treatment, but they are also effective for surface water treatment [221].

There are detailed studies on the adaptability of various plant species to CWs under changing water status [222]. Macrophytes such as *Commelina communis*, *Phragmites australis*, *Penniserum purpureum*, *Ipomoea aquatica*, and *Cyperus alternifolius*, all of them with a high rate of vegetative growth, are among the most commonly used in these wetlands [221,222]. Nitrate removal through CWs is mainly due to the presence of facultative anaerobic denitrifying microorganisms in their rhizosphere as well as their uptake by roots. [20]. CWs are ideal for nitrate removal, since they provide an anaerobic environment and fixed CO_2 as a carbon source for denitrifying bacteria. The estimated potential nitrate elimination rates are around 40–50 kg/ha/day [223]. Applications of CW for the denitrification of waterbodies include the rejuvenation of nitrate-contaminated aquifers, treatment of returning irrigation flows in hydroponic systems, groundwater treatment for industrial facilities, and treatment of nitrified wastewater effluents [223].

CWs are cost-effective compared to conventional treatment systems, are environmentally friendly, do not generate harmful by-products, and are adapted to the soil and climatic conditions of a particular ecosystem.

Microalgae cultivation is another nature-based solution for treating high-nitrate waters, which has gained wide acceptance as a water purification treatment method [20,224]. It is an interesting and cost-effective approach with the benefit of producing biomass that can be used for human food or animal feed and for the extraction of pigments and bioactive compounds. Microalgae, while consuming nutrients and CO_2, increase the dissolved oxygen in the culture bed, producing an algal biomass susceptible to be used in agriculture, livestock farming, or industrial extractive processes [225]. Nitrate ions are incorporated by the microalgae through an assimilation pathway and, in contrast to the bacterial denitrification process, no organic carbon source is required, as microalgae use the light to fix atmospheric CO_2 through photosynthesis [20]. For bioremediation of waterbodies by microalgae, factors as diverse as the simplicity of removal of microalgae from treated water, no release of organics, initial nutrient content, and N/P ratio need to be addressed [226,227].

The nitrate removal behaviour of freshwater microalgae viz., *Chlorella* sp., *Chlamydomonas* sp., *Scenedesmus* sp., *Ettlia*, sp. *Dunaliella* sp., and *Spirulina* sp. has been explored [226–228]. It has been reported that an optimal strategy for the bioremediation of groundwater is the mixed culture of *Chlamydomonas reinhardtii*, *Chlorella vulgaris*, and an *Ettlia* sp. in order to obtain maximum nutrient assimilation (73.5 g NO_3^-/L/day) and adequate settling efficiency [229]. The cultivation of *Dunaliella* sp. or *Spirulina* sp. is innovative, and is still at an early stage of research [228,230], but its great interest lies in the fact that it produces a biomass that will be used for food purposes and with a high added value due to its potential health benefits.

6. Final Remarks

Nitrate-related environmental problems concern all economic sectors and have a particular impact on aquatic ecosystems. It is a serious cross-border problem of global concern that must be decisively confronted because the negative effects are extremely evident in many areas of the planet, and in some of them, they are even bordering on irreversible.

The immediate step to address the problem of nitrate-polluted waterbodies is to control the main causative process; therefore, awareness should be raised to reduce nitrogen inputs to the soil to slightly lower levels than expected to obtain the optimum yield by applying less nitrogen fertilizer and further limiting livestock density. Treatment of waterbodies that already have excessive nitrate concentrations is also necessary to regenerate damaged ecosystems and reduce associated health hazards.

As we have described, different physical, chemical, and biological processes (ion exchange, reverse osmosis, adsorption, chemical reduction, biological denitrification, etc.) are known to be effective for denitrifying surface and groundwater bodies. Table 2 summarizes the main strengths and drawbacks of all of them. Table 2 does not go into capital investment and energy consumption considerations for the different technologies. Figure 11 groups them according to these two variables.

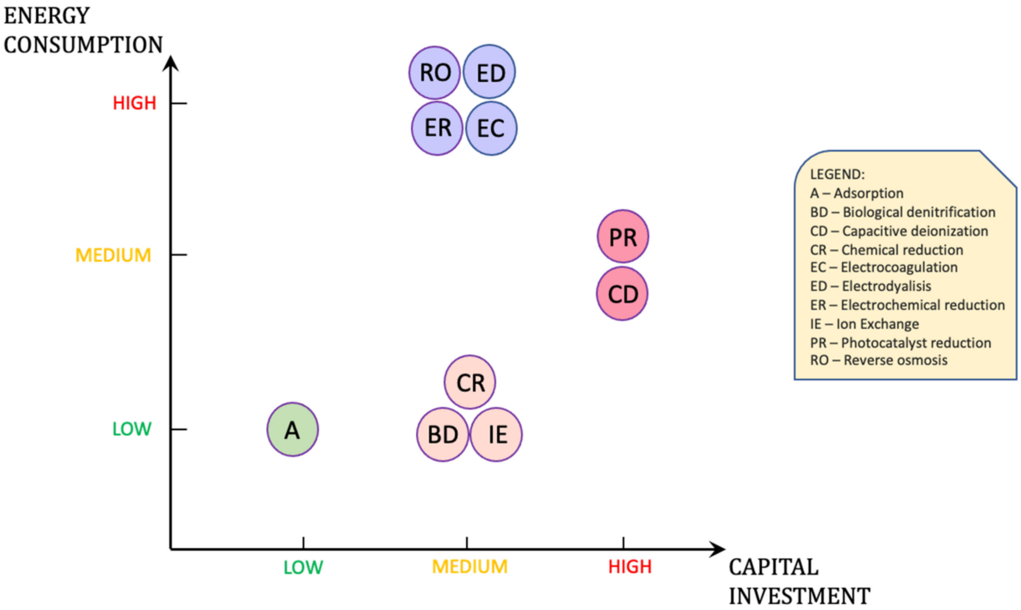


Figure 11. Categorisation of nitrate removal technologies according to capital investment and energy consumption.

Each of the technologies reviewed is certainly suitable in specific situations to achieve significantly high nitrate removal, but all of them suffer from drawbacks when they do not generate by-products and concentrated waste brines, consume a lot of energy, or have a high economic cost.

Table 2. Strengths and weaknesses of nitrate removal technologies.

Technology	Main Strengths	Main Weaknesses
Ionic exchange	Ion selective resins Insensitivity to temperature changes Automatic control	Generation of reject brine
Reverse osmosis	Stability over a wide pH range Multiple contaminant removal	Pre-treatment requirement Generation of reject brine High pressure is needed
Electrodialysis	Selectivity Low demand for chemicals	Pre-treatment requirement Generation of reject brine
Electrocoagulation	Operation at atmospheric pressure and ambient temperature	Anode passivation Sludge production
Capacitive deionization	Energy storage is produced	pH dependence Generation of waste concentrate Regeneration of electrodes Low selectivity Co-ion effects
Adsorption	Simple technology Multiple adsorbents	Adsorbent regeneration costs Activation requirement
Biological denitrification	Adaptable to multiple configurations	Temperature dependence Post-treatment requirement Odour problems
Chemical reduction	Flexible plants Elimination of multiple pollutants	Undesirable by-products Precipitation problems Potential for incomplete denitrification Post-treatment requirement Deactivation of catalysts
Electrochemical reduction	Treatment of drinking water Elimination of multiple pollutants	pH dependence Electrode passivation
Photocatalytic reduction	Green technology	Poor N_2 selectivity Inefficient photocatalysts for visible radiation Regeneration of photocatalysts

The main technologies applied commercially are the biological and ion exchange treatments. Ion exchange technology has long been the proven and reliable treatment route, with emphasis on the use of modern nitrate-selective anion exchange resins. Commercial biological treatments usually consist of fixed film bioreactors in which sand or carbonaceous particles are suspended or fluidized within the reactor by the upward flow of water through the system. The suspended medium provides a large surface area for microbial growth and allows for a high biomass density. The microorganisms in the reactor degrade all incoming nitrates under anoxic conditions. The use of membrane bioreactors and reverse osmosis plants is more focused on desalination processes of waterbodies that besides nitrates, also have a high content of other salts, either for agricultural purposes or to obtain drinking water [31,43,142].

7. Recommendations and Future Scope

There is a need to develop bio-based integrated hybrid processes for more efficient and cost-effective nitrate removal. The development of nanotechnology may have a role to play in this area. To date, there is no single technology that has an edge over the rest. It is a matter of optimizing and integrating available technologies or developing new green hybrid treatments that enable complete denitrification in a closed and controlled bioremediation system, free of secondary contamination. Green reduction technologies, such as constructed wetlands and microalgae cultivation, have gained much attention and show a progressive rise as a result of increased public awareness of environmental sustainability.

Untying environmental degradation from economic and social development is a permanent challenge and requires a paradigm shift at all social levels. There are pressing problems, such as nitrate contamination of waterbodies, which must be tackled urgently and decisively, and science must provide effective solutions because if there is no planet, there is no future.

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