

Mini-Review Article

Investigation of Nitrogen Removal in Municipal Wastewater Treatment Plants

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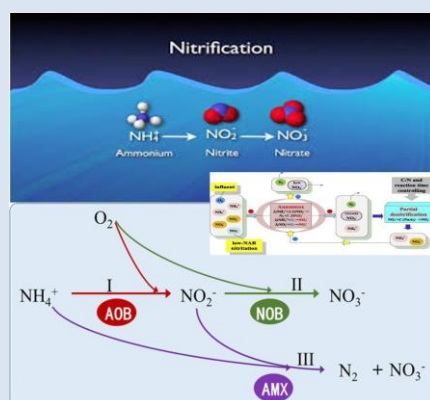
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Abstract: In general, the conversion of unstable organic materials in wastewater into stable minerals is one of the stages of wastewater treatment in a treatment plant. In other words, urban wastewater treatment plants try to purify municipal wastewater by converting organic materials into stable materials that have the ability to separate from wastewater. One of the most important organic compounds in municipal wastewater are nitrogenous materials and phosphorous materials that in municipal wastewater treatment plants. By nitrogen removal and phosphorus removal in wastewater, provide the possibility of municipal wastewater treatment. Although, the nitrogenous mineral compounds (nitrites and nitrates) and phosphorous mineral compounds are not the cause of contamination of treated wastewater due to their stability, due to their high nutritional properties, their entry into natural water sources greatly increases the growth and reproduction of aquatic organisms such as algae. In fact, phosphorus and nitrogen, because they are minerals, methods of separating nutrients from municipal wastewater in municipal wastewater treatment plants should be studied

Key words: Pollution; Wastewater; Wastewater treatment plant; Organic compounds; Nitrogen

Graphical Abstract:



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Introduction

Although the amount of nutrients generated by wastewater discharge may be less than that generated by waste of agricultural or other resources, the nature of the wastewater discharges makes their control techniques more appropriate. Therefore, wastewater treatment plants that discharge their effluent into the natural water sources, which have a special and delicate balance with food, are forced to limit the amount of nutrients in the effluent. The most important nutrients usually contain nitrogen and phosphorus [1-3].

Methods of Removing Nutrients from Municipal Wastewater

Considering the importance of separating nutrients (nitrogen and phosphorus) from the municipal wastewater and removing these substances from municipal wastewater, this important thing should be achieved in municipal wastewater treatment plants [4]. In general, the following separate methods are available for the separation of nutrients, especially nitrogen:

- Biological extraction (biological removal)
- Chemical methods
- Ion exchange

Although the above methods are available for the separation and removal of nitrogen and phosphorus from wastewater; however, in municipal wastewater treatment plants, separation by biological methods is usually used to separate and remove these materials from the field of operation [5].

In other words, for nitrogen and phosphorus separation in municipal wastewater treatment plants, the most cost-effective processes are processes for biological nitrogen removal and processes for biological phosphorous removal [6].

In addition to the mentioned biological method, nitrogen and phosphorus can be extracted from wastewater by the chemical methods and ion exchange; however, all these methods are rarely used in municipal wastewater treatment plants due to their complexity and high cost [7-9].

Biological Extraction of Nutrients

Separation of nutrients from wastewater before disposal is very important as nitrogen and phosphorus can affect the quality of wastewater. Therefore, controlling their disposal is essential [10].

Biological extraction of nutrients is a relatively inexpensive method of separating nitrogen and phosphorus from wastewater. Recent experiments have shown that biological processes are reliable and effective in the separation of nitrogen and phosphorus. Nutrient sequestration options that need to be studied are:

- Nitrogen separation without phosphorus separation.
- Phosphorus separation without nitrogen separation.
- Separation of nitrogen and phosphorus.
- Phosphorus separation during the year along with seasonal nitrogen separation.

Biological Processes of Nitrogen Removal from Municipal Wastewater:

Nitrogen removal in municipal wastewater (and wastewater in general) is treated and necessary before discharging it into receiving environments such as natural water sources, agricultural lands, rivers, and seas [11].

Nitrogen removal process is a necessary component to complete the refining operations and treatment of wastewater in municipal wastewater treatment plants. Removal of nitrogen from wastewater is a process that can be accomplished by biological wastewater treatment. Therefore, in order to do this, a sector is considered in treatment plants as other sectors, the purpose of which is to separate nitrogen from wastewater using biological processes and then to remove nitrogen (de-nitrogenation) from wastewater [12].

Types of Biological Processes for Nitrogen Removal in Municipal Wastewater Treatment Plants

The following are some of the common biological processes for the removal of nitrogen from municipal wastewater:

1. The anoxic/aerobic process (aerobic/deoxygenating)
2. Step-feed anoxic/aerobic process (aerobic / deoxygenated step processes)
3. Intermittent aeration (aeration periodic process)
4. Sequencing batch reactor
5. Denitrification (nitrate removal) after deoxygenation with the addition of methanol.

In this design example, process descriptions and flow diagrams for various de-nitrogenation removal processes as well as some design parameters are provided [13].

However, in general, in all biological processes of nitrogen removal, there are two main mechanisms, which are:

1. Nitrification (nitrate making)
2. Denitrification (nitrate removal)

In the municipal wastewater, nitrogen compounds are produced by the biodegradation of proteins and the depletion of urea from body wastes. This nitrogen may react with the complex organic molecules; in this case, instead of counting certain compounds, it is called organic nitrogen. Organic nitrogen can be biologically converted to free ammonia (NH_3) or ammonium ion (NH_4^+) under the influence of one of the various metabolic ways [14].

Nitrification Synthesis: To maintain the population of nitrate-making organisms in the microbial environment of activated sludge mixture, the minimum age of aerobic sludge $(\theta_c)_{\min}$ must be greater than the inverse of the net specific growth rate of the nitrate-makers:

$$(\theta_c)_{\min} \geq \frac{1}{\mu N_T - b N_T}$$

= Nitrate makers self-devouring death rate, d^{-1} , $b N_T$ which μN_T = specific growth rate of nitrate makings in terms of $\frac{g\Delta VSS_N}{(gVSS_N \cdot d)}$.

The growth rate of nitrate makers depends on the specific nitrification rate:

$$\mu N_T = a_N q_N$$

= Sludge product coefficient for nitrate makers a_N and d^{-1} = specific nitrification rate in terms of, N_q which the nitrification specific rate in activated sludge system depends on the concentration of output ammonia nitrogen and dissolved oxygen as well as PH. The

effects of dissolved oxygen and output ammonia are described as follows:

$$q_N = q_{N_M} \cdot \frac{NH_3 - N}{K_N + NH_3 - N} \cdot \frac{DO}{K_O + DO}$$

K_N and K_O are nitrogen and oxygen semi-saturation constants, respectively. The normal value is 0.4. K_O can vary from zero to 1 [15].

The effect of mixed liquid oxygen at the rate of nitrification is somewhat controversial because the concentration in the liquid mass is not the same as the concentration inside the clot where oxygen is consumed. Increasing the concentration of dissolved oxygen in the liquid mass cause's oxygen to penetrate into the clot and increase the nitrification rate [16].

In a reduced SRT, the rate of oxygen consumption causes more carbon to be oxidized, thus reducing the rate of oxygen penetration. Conversely, at high S RT, the lower the rate of oxygen consumption, the higher the amount of oxygen administered into the clot, resulting in a higher nitrification rate [17].

Therefore, in order to maintain the maximum nitrification rate, the oxygen concentration of the dissolved liquid in the mixed liquid should be increased by decreasing the SRT. This is reflected in the K_O coefficient [18].

In municipal wastewater treatment, the maximum specific nitrification rate should be determined experimentally [19]. The dependence of the specific nitrification rate on temperature is given by the following relation:

$$q_{N(T)} = q_{N(20C)} \times 1.09^{T-20}$$

The self-devouring coefficient b_N has a heat coefficient of 1.04:

$$b_N = b_{N(20C)} \times 1.04^{T-20}$$

The nitrogen to be oxidized can be calculated from the following equation:

$$N_{OX} = TKN - SON - N_{syn} - (NH_3 - N)_e$$

Where S_{ON} = non-degradable organic nitrogen and $0.08 a_{S_r} = N_{syn}$ nitrate making component can be calculated as follows:

$$f_N = \frac{0.15 N_{OX}}{a_{S_r} + 0.15 N_{OX}}$$

The total nitrification rate is:

$$R_N = q_N f_N X_{vb}$$

R_N is the nitrification total rate in mg/(L.d).
The retention time required for nitrification is equal to:

$$t_N = \frac{N_{OX}}{R_N}$$

To determine the SRT, it is necessary to calculate the excess sludge (WAS):

$$\Delta X_{VB} = (a s_r + 0.15 N_{OX}) - b X_d X_{VB} t_N$$

And SRT is equal to:

$$\theta_C = \frac{X_{vb} t_N}{\Delta X_{vb}}$$

The required oxygen is equal to:

$$O_2 = 4.33 N_{OX}$$

And the required alkalinity in terms of CaCO_3 is equal to:

$$ALK = 7.15 N_{OX}$$

Anamox Process for Nitrogen Removal

Microbial processes have the greatest impact on the nitrogen cycle in aquatic environments such as the oceans [20].

In this study, the anaerobic oxidation process of ammonia is investigated. Humans have altered the nitrogen cycle by producing fertilizers, burning fossil fuels, extensive agricultural activity, and other activities [21].

Of course, the rapid acceleration of the nitrogen cycle has made food production possible for the world's population, but today it has also become an environmental problem. Because nitrogen is a useful nutrient, changes in its amount make a difference in ecosystem production and competition between It becomes different species. Nitrogenous compounds such as nitrogen monoxide and dinitrogen oxide react with ozone in the troposphere and pollute the air [22].

In addition, due to the declining capacity of the oceans to provide the protein needed by humans, production in this sector has increased. Solving the problem of the nitrogen cycle in aquatic environments is a challenge that we are facing today. Nitrogen flux in these environments is controlled by biological processes. On the one hand, diazotrophic microorganisms are responsible for the stabilization of nitrogen in the

oceans, and on the other hand, nitrification processes, and denitrification are known to be the main factor in nitrogen removal [23].

Recently, anaerobic oxidation of ammonia (Anomox) has also been suggested as one of the nitrogen removal agents. This process removes ammonia nitrogen using nitrite as the electron acceptor [24].

Anomax Process

Anomax is a biological process that converts ammonia to nitrogen gas under the anaerobic conditions, using the nitrite as the electron acceptor. The discovery of this process changed the perception of nitrogen removal. Prior to the discovery of this process, it was the only known microbial process for nitrogen removal. Austrian scientist Angelbert Broda had predicted the existence of the Anomax process by thermodynamic calculations. In the Netherlands, this process was also observed in a mobile bed bioreactor during the treatment of fermentation wastewater. The discovery of Anomax has attracted the attention of many researchers around the world. This process involves microorganisms, especially bacteria, found in soil, groundwater, sewage, marine sediments, ponds, and low-oxygen areas [25].

Microbial Diversity

Today, the development of Anomax bacteria in wastewater treatment systems is done and due to the low growth rate of these bacteria, special attention has been paid to the preservation of its biomass. In order to advance Anomax, various processes have been launched, including continuous batch reactors, upstream sludge bed, rotating biological disks, and membrane bioreactors [26].

Today, 10 species of Anomax have been identified, including 7 improved culture media. It should be noted that none of the Anomax species is a pure species, but a mixture of different microorganisms that are divided into 5 general categories. These categories include *Quanina*, *Brocadia*, *Anomaxoglobus*, *Gatenia*, and *Scalindova*. The first four types of sewage treatment plant sludge are separable, but the latter species are found in aquatic environments, clean water ecosystems, and treatment plants [27].

The development of the anomax process is more related to planktomyces. Due to their unique physical, chemical and biological properties, Anomax bacteria have their own special family called brocadial. To fully identify these organisms, special tools have been developed that use 16 renatin reins and functional genes as biomarkers. Molecular methods mostly show the presence and absence of Anomax bacteria, while isotopic methods can be the best option to investigate nitrogen removal by the Anomax process [28].

Specific Cellular Characteristics

Planktomycetes are regular, fragmented cells, so Anomax bacteria have one thing in common. Anomax cells are made up of three parts, each bounded by a membrane. The outermost region of the cytoplasm, which is associated with the cell wall and cytoplasmic membrane, contains peptidoglycans [29].

The second region is the nucleoids and ribosomes, which are similar to the cytoplasm of prokaryotes, where the transfer and translation of metabolic activity occurs [4].

The third region is called the anomaxosome, which covers most of the intracellular space, and is the preferred region of the anomax bacteria. Scientific reports show that this structure inherently belongs to the daughter cell during reproduction. One of the special features of Anomax bacteria is the composition of their cell membranes. The glycerolipids of these bacteria are a combination of ester, ether, fatty acids, and long-chain alcohols [31].

In particular, the membranes of Anomax bacteria contain 17 and 18 carbon saturated fatty acids and alcohols that form cyclo-butane and cyclohexane ring-shaped ladders by cis-ring bonding [32].

Biochemical Properties

According to the early metagenome of Anomax bacteria, there are three main reactions involved in the metabolism of these substances, the main of which are hydrazine and nitrogen monoxide. Kartal et al. [5] determined the metabolic pathways of the anomax process in the laboratory. Enriched culture medium of *Castotgartinsis* was used to determine these mechanisms by transcriptomic, proteomic, inhibitory and isotopic experiments. This culture medium was able to reduce nitrite to nitrogen monoxide and with the property of green fluorescence, the production of nitrogen monoxide was proven.

Reduction of nitrogen monoxide and its conversion to hydrazine was also confirmed. The path of this process then ends with the oxidation of hydrazine and its conversion to nitrogen gas. Recent research shows that there is a great deal of metabolic variation in the production of nitrogen gas by anomax bacteria, and at least two known metabolic pathways in which anomax bacteria convert ammonium to nitrogen gas.

Anomax Process in Aquatic Environments

Microorganisms in aquatic environments are responsible for half of the earth's primary production and play an important role in the global food cycle. The first evidence of this process was reported by TomDrop and others. For this purpose, they used nitrogen chase analysis in a coastal area of Denmark. Kuipers et al.

Then estimated that at least 30% of nitrogen conversion occurs in the Black Sea. At the same time, Dalsgaard and the rest witnessed the high activity of Anomax in the coastal Gulf of Costa Rica.

Other studies have measured the overall level of nitrogen production, especially in estuaries. Nitrogen production in these studies ranged from 0 to 79% and in some cases the Anomax process was not involved (Table 1). The only bacteria found in the sultry, tropical and anaerobic regions belonged to the *Candida scalindova* gene. These gene sequences have also been found in various regions, such as the Black Sea. Compared to other areas, the Anomax process occurs less frequently in aquatic environments. The population of anomax bacteria has been found in deep areas such as sulfide ponds in the eastern Mediterranean [33].

Contribution of Ammonium Anaerobic Oxidation in Biogeochemical Cycles

Nitrogen flux is controlled by broad groups of microorganisms in oceanic environments. While diazotrophic microorganisms stabilize nitrogen and are a source of nitrogen storage for carbon sequestration, the denitrification process is a major source of nitrogen return to the atmosphere.

Of course, the Anomax process is also known as a major nitrogen well and removes up to 50% of nitrogen. The occurrence of the Anomax process creates an ecosystem so that nitrite and ammonia are present at the same time. Although the share of Anomax in the whole denitrification process is about 80%, the nitrite concentration in many sediments is small. This phenomenon is due to the occurrence of microbial reactions and changes in the presence of microorganisms in different seasons of the year. A constant amount of nitrogen usually limits the production of biomass in the oceans and seas and therefore reduces the consumption of carbon dioxide by phototrophs, which has a positive effect on global warming. Thus, access to this important food source not only affects the functioning of the oceans, but also the global biogeochemical cycles.

The global nitrogen fixation rate is about 100 to 200 tegrans per year, which must compete with major nitrogen wells (anomax and denitrification). Annual denitrification removes 200 tragrams of nitrogen. In addition to denitrification and anomax, other cycles affect nitrogen production and consumption, including sulfamox, fimax, and anomax dependent on natural organic matter [34].

Reduction of sulfate produces high concentrations of ammonia in the sediments, which is due to the mineralization of natural organic compounds. The presence of sulfate as the final electron acceptor in

these precipitated media creates a barrier resulting from sulfamox reactions to prevent ammonia from entering the anaerobic areas where anomax and denitrification occur. The recently known Fimax process significantly reduces nitrogen in aquatic environments and overshadows the nitrogen balance in these environments. Thus, the biogeochemical interaction between the Sulfamox, Fimax and Anomax processes is much more complex than previously thought. In addition to the processes that consume nitrogen, there are also processes that produce nitrogen [35].

Anaerobic oxidation of ammonia

The discovery of the anaerobic oxidation process of ammonia dates back to 25 years ago and changed the world view of the biogeochemical cycle of nitrogen. In addition, Anomax bacteria have metabolic variability, for example iron and manganese oxides are formatted as electron donors by caustic gartensis. In 2008, Van et al. Discovered the use of nitrate-dependent formate, acetate, and propionate. In addition, Anomax bacteria can use ferrous iron, methylamine, and hydrogen for respiratory ammonification. There are different electron receptors for nitrite in the anomax process. One of these electron receptors is ferric iron. This substance is also present in the Fimax process. Another method for anaerobic oxidation of ammonia is to reduce sulfate. Other methods include reducing natural organic matter to remove ammonia, which has recently attracted the attention of researchers. These processes are briefly discussed below.

Fimax Process

Anaerobic oxidation of ammonia, which is associated with the process of reducing trivalent iron, was first discovered in 2005. Clement and others observed this process in the soil of Wetland. During incubation of the sludge they took from the soil, they noticed the unexpected production of divalent iron and the production of nitrate. This process was then named Fimax by Sioma, and it was noted that trivalent iron-reducing bacteria can convert ammonia to nitrite, in a solution of trivalent iron chelated by EDTA. The Fimax process with nitrogen production is better in terms of energy than the Fimax process with nitrite and nitrate production as end products. Little is known about the occurrence of Fimax in oceanic environments. However, a recent report has been published in two types of ocean sediments of the Phimax process, one of which uses free carbohydrates and the other ferric iron. Analysis of nitrogen tracer materials showed that this process releases up to 2 micrograms of nitrogen per gram per day, indicating that they are a suitable process

for nitrogen wells in areas with hypoxia. In fact, the use of nitrogen by the Fimax process in these areas is comparable to arid areas.

Sulfamox

While anaerobic oxidation of ammonia, which is associated with sulfate reduction, has been reported in some wastewater treatment systems, this process also occurs in nature. Sulfate is the largest electron acceptor in aqueous media and has been used as the main cause of anaerobic oxidation of nitrate for many years. Scrum and others studied the thermodynamics of sulfate reduction and ammonia oxidation in the Bay of Bengal. They checked the chemical profiles of the water to make sure the process was happening in nature. Recent stoichiometric analysis and trace elements of nitrogen have shown that this biological process also occurs in sediments in northern Mexico. Spectroscopic evidence shows that this process produces other products, including elemental sulfur, sphalerite, and free sulfide.

Anomax dependent on natural organic matter The natural organic matter in the ocean is one of the largest reserves of carbon on Earth, estimated at 662 petagrams. Thus, the sediments of many coastal areas that receive water rich in organic matter are a potential source of organic carbon. Wet materials are high in natural organic matter. These materials have previously been used as the main and last electron acceptor in the oxidation of methane, phenolic compounds, hydrocarbons and other organic pollutants. Depending on the electron acceptance capacity of natural organic matter, these materials can participate in the anaerobic oxidation process of ammonia as an oxidizing agent. Natural organic matter is inherent in marine sediments and causes nitrogen consumption to increase from 0.4 micrograms per gram per day to 1.5. Other documents also confirmed the oxidation of ammonia with the help of natural organic matter. Spectroscopic results also confirmed a decrease in electron acceptor groups such as quinone.

In addition, human microorganisms can oxidize a wide range of materials, including methane, hydrocarbons, and halogenated solvents. Therefore, there is a good potential for generating electricity by biological processes.

Anaerobic nitrogen oxidation technologies in wastewater treatment

One of the special applications of the anaerobic oxidation process of nitrogen is wastewater treatment. The presence of ammonia in wastewater poses dangers to aquatic life and organisms; therefore, the removal of this substance from wastewater is essential, which is

further addressed in its various technologies by anaerobic oxidation of ammonia.

Anamox

The Anomox process was detected in a wastewater treatment system. Therefore, the use of this process in the removal of nitrogen from wastewater is obvious. The Anamox process is a good alternative to nitrification and denitrification because it is more economical and requires less energy. Of course, there are challenges to using this process. The biggest problem is the slow growth rate of microorganisms, which takes between 7 and 14 days to double, causing the startup to slow down the process on an industrial scale. Although the slow growth rate of microorganisms reduces the volume of sludge produced, it becomes problematic to start the process without special culture. Although the Anamox process is newly recognized, 110 units on an industrial scale have been established worldwide to date. Of course, most of these units are established in Europe (84 out of 110 cases). The rest of the challenges have been resolved so far. For example, the first Anamox unit had a volume of only 70 cubic meters, but large-scale units have been established that have a volume of 142,000 cubic meters and remove 134 tons of nitrogen per day. Various systems drive the Anamox process, including a continuous batch system, a gas lift, a membrane bioreactor, biological rotating disks, and an upward-flowing anaerobic sludge system. There are two ways to reduce the startup time of the Anamox process. In the first place, the appropriate reactor configuration must be selected, and the second solution is to keep the resulting biomass in the reactor to advance the anamox process.

An overview of nitrate removal strategies from water using nanotechnology

Nitrate is one of the water pollutants that its removal from water is necessary to reduce pollution and prevent damage to the life of living organisms. Conventional methods of nitrate removal from water such as adsorption, ion exchange process, reverse osmosis, electrochemical, chemical and biological methods face several limitations such as high installation and execution costs, multiplicity of steps and low efficiency. Nanotechnology has been used effectively in many environmental applications, such as the use of nanomaterials to regenerate soil and water, remove wastewater contaminants, and treat fresh water. Recently, nanotechnology has been considered as an excellent alternative to conventional nitrate removal methods. Nanomaterials are highly reactive due to their small size and high surface-to-volume ratio, which enables them to be used as adsorbents. In this review

article, we will examine the applications of various nanomaterials, especially nanoparticles, nanotubes, nanofibers, nanoclusters and synthetic nanoparticles to remove nitrate from water. The advantages, disadvantages, limitations and advantages of using these nanoparticles will also be discussed.

Water pollution is a major problem and has many consequences on life on Earth. This type of pollution is mainly caused by industrial pollution and human activities. In the last 200 years, there have been significant changes in the global nitrogen cycle. Nitrogen concentration and mobility are increasing in large areas of the earth. In addition, through various human activities such as the use of pesticides, the use of organic or inorganic compounds, improper disposal of industrial waste, discharge and infiltration of waste into groundwater and wastewater containing inorganic nitrogen such as nitrate (NO_3^-) enters urban and agricultural runoff Aquatic ecosystems become the environment.

International standards define the concentration of nitrate in water, and increasing the concentration of nitrate more than the desired level in water sources has become an environmental concern around the world. There is a high volume of nitrate in the water and it also penetrates the sources of drinking water. Accumulation of nitrate in the body at high concentration levels is known to be the cause of many complications including methemoglobinemia and diabetes. Also, marine organisms, especially freshwater ecosystems, are more affected by the presence of excessive nitrate in the water and the resulting poisoning. Nitrate removal from environmental sources such as surface water and groundwater is one of the requirements to prevent such complications. There are several common methods for removing nitrate from effluents, including adsorption-based methods, ion exchange process, electrochemical method, reverse osmosis, biological methods and chemical methods. However, these techniques have several limitations. One of the limitations of adsorption-based techniques is the changing conditions of the aqueous environment, which makes it difficult to select a high-efficiency adsorbent that fits different environmental conditions. Estimation of adsorption efficiency, ability to reduce adsorbent for multiple uses, and recycling of adsorbent with adsorbed nitrate are among the limitations of conventional adsorption-based techniques. In the ion exchange method, there are limitations such as the application of anterior and posterior treatments. Reverse osmosis in the presence of other impurities, shows a decrease in efficiency and effectiveness. Also, this technique requires a certain amount of water pressure and also the devices used are prone to saturation and filling with biological agents such as algae and bacteria in wastewater. Biological

and chemical methods also cause toxicity in water. Also, the equipment associated with these methods is very expensive. Nanotechnology-based techniques have been introduced as a viable alternative to conventional methods.

Nitrate removal mechanisms

Nitrate is usually formed in nature as a product of nitrogen denitrification and is highly soluble in water, inactive and non-reactive. Chemical fertilizers and other wastes containing nitrogen decompose and are converted to nitrate and nitrite by further oxidation of ammonia. Nitrate is present in air, water and food and is synthesized by plants into organic compounds. Nitrate is one of the factors that, when combined with moisture, produces nitric acid. Although inactive, it is microbially reduced to nitrogen gas (N_2) and nitrogen monoxide (N_2O). Common commercial reducing agents include active metals, ammonia, borohydride, formate, hydrazine, hydroxylamine, hydrogen, and iron. Active metals reduce nitrate to ammonia or nitrite in neutral pH environments, while active metals reduce ammonia to nitrate and nitrate to nitrogen or nitrous oxide at high pressures and temperatures and in acidic environments. Sodium tetrahydroborate in the presence of metal alloys forms nitrite and ammonia. Reduction of nitrate is possible by methods of adding energy to the reaction medium such as electrochemical, thermal or photocatalytic methods. However, simple chemical reduction reactions in microenvironments do not effectively remove nitrate. Nitrate reduction is possible in the presence of a strong catalyst. Nanomaterials have significant catalytic properties due to their surface properties. In the nitrate reduction process, ammonia (NH_3), nitrogen gas (N_2), nitrite (NO_2^-) and ammonium (NH_4) are formed. The products of the nitrate reduction reaction vary depending on the type and size of nanoparticles used. Another common mechanism for nitrate removal is adsorption-based techniques. In the adsorption method, nitrate molecules are attached to the surface by physical adsorption or by adsorption due to chemical interaction. Nanomaterials that have excellent adsorption properties have two main properties; The inner surface is wide and the outer surface is functional. Extensive active surface, adsorption activity, structure and location of atoms at the nanoparticle surface, absence of diffusion resistance into the nanostructure and high bond energy are the factors determining the capability and efficiency of nanoparticles. The adsorption ability of nanoparticles has been investigated using both isothermal and kinetic models.

Nanomaterials for Nitrate Removal

The nano materials used to date for nitrate removal are nanoparticles, nanotubes, nanofibers, nano clusters, and nanocomposites. Nanoparticles have a variety of environmental applications such as contamination detection and concentration monitoring, chemical decomposition or environmental remediation. Nanoparticles have the ability to remove a wide range of contaminants. Nanoparticles can be used as reducing agents or as adsorbents for various contaminants in soil or water. Nanoparticle-based techniques have been proposed as a suitable alternative to conventional methods for nitrate removal from effluents due to their diverse properties such as small size, high surface-to-volume ratio and optimum catalytic activity. Due to the high efficiency of these nanoparticles, these systems can be used alone and there is no need for complementary systems. These nanoparticles are used in coated or functionalized forms and to stabilize nanoparticles on the surface.

Iron nanoparticles

Zero-valent iron nanoparticles (NZVI) have attracted the attention of the international scientific community due to their excellent catalytic properties and high surface-to-volume ratio. These properties enable this type of nanoparticle to be used as a reducing agent. NZVI has also been used as an adsorbent in some studies. NZVI nanoparticles are widely used for nitrate removal without any application of surface modifications. In an NZVI research project, hydrothermal and natural goethite was synthesized through a natural reduction process. However, the synthesis of NZVI is an expensive process. When natural goethite and hydrothermal are used as raw materials, the synthesis process becomes cheaper. The removal efficiencies of NZVI nitrate synthesized with natural and hydrothermal goethite and NZVI synthesized with common and expensive raw materials were compared. Normal NZVI shows a removal rate of 90% at pH 1, but the removal rate was significantly reduced to 10% at pH 6, while NZVI obtained from natural and hydrothermal goethite had a removal rate of 95.1% and 91.3%. Showed 100% at pH 1 and this amount decreased at pH 8. to 72.4% and 83.5%. Increasing the initial nitrate concentration also affects the nitrate removal rate. In the nitrate removal process over time using NZVI synthesized from natural goethite, an increase in ammonia formation was observed, while very small concentrations of nitrite were formed. During the process, some nitrate was reduced to nitrogen gas. NZVI synthesized using natural and hydrothermal goethite is a cheap, high-efficiency alternative to nitrogen removal for conventional zero-capacity iron.

In another study on nitrate removal by NZVI, the efficacy of newly synthesized NZVI, dried NZVI, and sonicated NZVI was investigated. Nitrate reduction was performed using these NZVIs under different conditions such as pH, initial nitrate concentration and different adsorbent doses. Changes in pH had no significant effect on nitrate reduction. NZVIs break down nitrate into ammonium and nitrite. However, the amount of nitrite produced was low and decreased over time. In the case of fresh NZVI, nitrate was reduced at a faster rate of 1 mg / ml nitrate per minute. In the treatment using fresh NZVI, nitrite production increased to 5% for 20 minutes. And in the case of dried and sonicated NZVI, nitrite production reached almost 7%. In another study, NZVIs doped with gold, copper, and silver nanoparticles were fabricated and used to simultaneously remove nitrate and cadmium (Cd) contamination. In this study, the reactivity of NZVI to the composition of composite pollutants and the effect of production and the presence of by-products on nitrate removal efficiency were evaluated. During the experiment and over time, it was observed that the reduction of nitrate increases the pH and iron oxide is formed and iron ions are not released. Also, during the test, the negative charge of the NZVI level increases. In the absence of cadmium (II) in the reaction medium, about 30% nitrate was reduced, but in the presence of cadmium (II) at a concentration of 40 mg / l, nitrate was completely removed. From these results it can be inferred that increasing the cadmium accumulation areas at the NZVI level increases the nitrate removal efficiency. In the presence of a concentration of less than 40 mg / l cadmium (II) and 20% of the initial nitrate concentration, a significant amount is converted to ammonia. NZVI is combined with other nanoparticles to increase nitrate removal efficiency. In one study, NZVI conjugation with magnetic nanoparticles was used to remove nitrate from groundwater. Nitrate removal efficiency using this type of conjugated nanoparticles was reported to be very high and desirable. The increase of magnetic nanoparticles and the increase of nitrate removal efficiency from water are linearly related to each other. Due to the magnetic nature of the magnetite nanoparticles, they are uniformly dispersed on the surface of NZVI. These nanoparticles increase the gradual process of NZVI corrosion and facilitate electron transfer to reduce nitrate through NZVI. Ordinary water shows a higher rate of nitrate reduction than distilled water, which can be mentioned as the reason for the increase in the rate of nitrate reduction at the joint surface of water and NZVI. Other possible reasons include an increase in the level of the complex at the molecular level of contact with the cations in the reaction medium. Conjugation of magnetic

nanoparticles with NZVI also increases the stability of this type of nano system and allows the completion of all four nitrate cycles.

NZVI without modification and also in conjugation with other nanoparticles shows good results in reducing nitrate and removing this contaminant, but the problem of agglomeration is one of the main challenges and overcoming this challenge is one of the important issues in the application of nitrate removal techniques based on this. It is a type of nanoparticles. Accumulation of NZVI nanoparticles affects nitrate removal efficiency. One way to overcome this challenge is to fix the nanoparticles on the base surface. Other solutions include metal-doped nanoparticles and the use of suitable materials to cover part of the surface in order to stabilize and increase nitrate removal efficiency.

Stabilization of NZVI on the surface increases nitrate removal efficiency. In one research paper, NZVI was stabilized on the surface of Macro porous Alginate (MAS). This new nano system has the ability to remove more than 96.5% nitrate in 30 minutes. The nitrate removal efficiency of NZVI nanoparticles without any surface changes is only 44.7%. By comparing the efficiency of these two types of nano systems, it can be concluded that the stabilization of NZVI on the surface has a significant effect on the efficiency. Also, the quality of the reaction performed by NZVI is significantly different when stabilized and free. In the case of stabilized NZVI, after 30 minutes with continuous ammonium addition conditions, nitrite remained in the reaction medium and 5% nitrogen gas was released. Under high pH conditions, nitrite and ammonium were produced while the concentration of ammonium gradually decreased in the environment. MAS levels prevent NZVI aggregation and agglomeration and increase redox activity. Graphite has been reported as another suitable surface for NZVI stabilization. This nano system is used to remove nitrate by reducing chemicals. In a research paper, KBH₄ was used as a reducing agent in water and ethanol to form NZVI nanoparticles. This experimental project was performed to study the effect of the combination of these particles in the reduction of nitrate. Under neutral pH conditions, 80 mg / L nitrate stabilized by NZVI was removed for 30 min. The high surface-to-volume ratio of graphite facilitates the dispersion of nanoparticles and prevents the compaction and agglomeration of NZVI nanoparticles. The main products of the nitrate reduction reaction for this nano system were nitrite and ammonium. Nitrite is formed in small amounts and slowly disappears completely. The reduction process is highly pH dependent and is amplified at an acidic pH. Graphene has also been used as the NZVI stabilization

surface and the NZVI / Nano graphene nano composite has been investigated. XRD (X-ray diffraction) measurements showed that un-stabilized NZVI had little stability, but stabilization on the graphene surface greatly increased the stability of NZVI and also prevented the absorption of electrons from the environment and the oxidation of NZVI. Most nitrate ions were removed from the medium using this nano system with a nano composite mass ratio of 25 / NZVI / Nano graphene. NZVI stabilized on the graphene surface showed a 125% increase in nitrate removal efficiency compared to NZVI free. The experimental results on this nano system showed a significant effect of acidity on improving the reduction process.

Using this nano system, most nitrate ions are discharged into the reaction medium within 16 hours. The use of ultrasonic in the reaction medium reduces this time to three hours. The mechanism of nitrate reduction is that first the nitrate ion is reduced to nitrite or ammonium and then the reaction is converted to nitrogen gas. Nitrate removal has three main steps; Adsorption, reduction and evacuation. In the case of this nano system, acidic conditions are also very favorable for reducing ammonia to nitrate. Stabilization of NZVI on graphene significantly increases nitrate removal efficiency, which can be attributed to increased surface area and stability and prevention of agglomeration. Another strategy to increase nitrate removal efficiency is the use of bimetallic nanoparticles. This type of nanoparticles makes it possible to remove nitrate in the presence of several high-efficiency contaminants. For example, Fe/Ni (iron/nickel) nanoparticles were synthesized and fixed on the kaolin surface and used to remove nitrate in the presence of copper ions. A certain ratio of kaolin, iron, nickel (K-Ni/Fe) was fixed on the kaolin surface. By increasing the amount of copper ions with concentration (100 to 200 mg/l), the nitrate removal efficiency improved from 26.9% to 40.4%. Possible mechanisms for increasing efficiency include the adsorption of ions on kaolin or iron oxide and the increase in denitrification due to the formation of a new trimetallic catalyst (Fe/Ni/Cu). NZVI bimetallic nanoparticles also have the ability to remove nitrate faster than NZVI bimetallic nanoparticles. In another study, iron-palladium (Fe/Pd) nanoparticles were investigated for nitrate removal. NZVI has the ability to reduce nitrate to nitrite and ammonia, and palladium exacerbates the reduction of nitrite to non-toxic nitrogen gas. To increase the efficiency of bipolar nano systems, these nanoparticles are fixed on Fe / Pd chelating resin. These types of nano systems are made in two ways. In the first case, NZVI is fixed on the resin and then palladium is dispersed on it. In the second case, first palladium is fixed on the surface of the resin

and then NZVI is fixed on it. Bimetallic nanoparticles convert nitrate to nitrite and ammonia, and in the next step nitrite is converted to nitrogen or ammonium gas. However, the conversion of nitrite to nitrogen gas requires the adsorption of hydrogen gas on the palladium surface; therefore, the amount of palladium loaded is directly related to the amount of nitrogen gas produced. It was also observed that increasing the pH of the solution increases the production of nitrogen gas. The optimum pH was 8.63, at which the highest selectivity for N₂ was observed. It was also observed that palladium and pH both have a synergistic effect on each other. The observations showed that the catalyst weight contained 8% NZVI and 8% palladium at pH 8.67 and the selectivity of N₂ reached 71%.

The final and desirable product in the nitrate removal process is non-toxic nitrogen gas. In another paper published in this field, a combination of three metals, copper, palladium and NZVI, was investigated as a nitrate removal nano system. The compounds (Cu-NZVI, Pd-NZVI, Cu-Palladium NZVI and Pd-Cu-NZVI) were synthesized by chemical reduction and their efficiency for nitrate removal was tested. The size of the synthesized nanoparticles was in the range of 20 to 150 nm. The Pd-Cu-NZVI trimetallic catalyst with a Pd: Cu ratio of 2: 1 showed the highest nitrate reduction at 63% and the NZVI base state showed a nitrate removal efficiency of 56%. 2: 1 showed the highest selectivity for N₂: NH₄ formation. NZVI acts as an electron donor to Cu and Pd metals and interacts with molecules in the reaction medium to synthesize hydrogen gas. Nitrate, in the reaction medium, nitrate is adsorbed to the surface of copper and interacts with hydrogen and is reduced to nitrite, then the reaction is reduced by adsorption of hydrogen on the surface of palladium nitrite to ammonium and hydrogen gas. By stabilizing the combination of two and three metal nanoparticles with NZVI on the surface, the nitrate removal efficiency of this type of nanosystem can be increased. NZVI, Cu, Mn, Cu/Fe and Mn/Fe compounds were prepared and fixed on the surface of NaY zeolite in a research study on the nitrate removal efficiency of this type of nanosystem. How zeolite is made has a significant effect on the efficiency of the nanosystem. Natural or synthesized zeolite affects the composition and catalytic activity of stabilized metals. These structures have the ability to selectively exchange ions with ammonia and at the same time prevent the release of ammonium into solution. Zeolite composites with nanoparticles fixed on their surface showed a 100% efficiency of nitrate removal from the liquid medium after six hours. The probable reason for this extraordinary efficiency is the loading of nanoparticles and the stabilization of both the connection to the base surface and the connection to the

inner layer during the preparation of the composite. Nitrate removal rate increases with increasing concentration of composite metal nanoparticles fixed on zeolite. One hundred percent efficiency was observed by this nanosystem with a concentration of 4 g/l composite. This composite nanostructure showed higher efficiency than metals alone. Nitrate removal by this nanosystem does not depend on acidic or alkaline conditions, and this type of nanostructure had a constant nitrate removal efficiency in both acidic and alkaline conditions.

Coating NZVI with a coating chemical or a layer of carbon monoxide is another strategy that has been investigated by NZVI to improve nitrate removal efficiency. Nanoparticles of iron, nickel and cobalt were coated with graphene oxide. This type of coating prevents agglomeration and increases the stability of the nano system and also improves the nitrate removal efficiency by this system. Stabilized nickel iron and cobalt nanoparticles on graphene oxide and increases the nitrate removal efficiency from water. Properties such as high stability, high surface to volume ratio, high oxidation potential and favorable magnetic properties make graphene a suitable option for use in water remediation. Both sides of graphene sheets can be functionalized. Different functional groups can be placed on its surface and this type of nanoparticles can be used in various applications. The negative surface charge of graphene allows dispersion and stability in the mineral environment. Proper dispersion is a key parameter for the nitrate reduction process. The nitrate removal rate after eight hours for graphene-stabilized nanoparticles was 90% for iron, 83% for nickel and 81% for cobalt, respectively.

In another research paper published by Wang et al., Fe nanoparticles were synthesized using eucalyptus and green tea extract and then coated with polyphenols and used to remove nitrate. Iron nanoparticles synthesized with eucalyptus extract showed a nitrate removal efficiency of 59.7% and iron nanoparticles synthesized using green tea extract showed a nitrate removal efficiency of 41.4%.

NZVI gradually loses its reactivity over time, despite its highest nitrate removal efficiency. But iron nanoparticles synthesized with plant extracts retain their reactivity even after two months. Nitrate removal kinetic studies for iron nanoparticles synthesized with plant extracts were investigated using the pseudo-second adsorption model and the best value for q_e constant (adsorption capacity in equilibrium) was 13.06 mg / g and 9.698 mg / g for synthesized iron nanoparticles. Were calculated with green tea and eucalyptus.

Another study on the effect of duration and novelty of the synthesized material on nitrate removal efficiency

used chromium-coated NZVI nano system. In this research paper, NZVI nano systems were coated with chromium in three newly synthesized, dried and sonicated modes and the effect of this type of coating on the nitrate removal efficiency by this nano system was investigated. NZVI was used as a control in three forms: freshly synthesized, dried and sonicated. The newly synthesized chrome-plated NZVI was highly active, reducing about 10 to 10,000 ppm in one minute. Dried NZVI, dried and chromium-coated NZVI showed less reducing activity than sonicated NZVI. It can be inferred that the reason for this type of behavior and difference in performance is related to the agglomeration parameter.

Metal nanoparticles and metal alloys

Metal nanoparticles and metal alloys have high surface to volume ratio and optimal conductivity properties. Many catalysts are made of metal nanoparticles. In the process of reducing nitrate, a promoter is needed. The promoter and catalyst reduce nitrate to nitrite by the redox process and further reduce the reaction of nitrite to nitrogen gas. The properties and catalytic activity of this type of nanoparticles depend entirely on the size and morphology of the nanoparticles. For example, Pt nanoparticles (Pt) have desirable reduction properties. These properties depend on the shape and size of Pt nanoparticles. During the studies, Pt nanoparticles with morphology of (100) Pt and (110) Pt were synthesized by electro deposition method and the effect of morphology on nitrate removal was studied. Rotational voltammetry was performed in solution with a nitrate concentration of 50 Mm and a scan rate of mV/s. Nitrogen reduction was considered to be mediated by complex formation and then ammonia formation. Scanning at a higher rate of nanoparticles (100) Pt compared to (110) Pt showed higher efficiency in nitrate removal. Platinum nanoparticles in the form (110) Pt did not show good reactivity. Aluminum oxide (Al₂O₃) nanoparticles such as nano alumina in the form of nano powder can be used to remove nitrate from water. During studies and experiments, nano alumina with a concentration of 10 to 20 mg / l showed better nitrate absorption. Maximum nitrate removal occurs at a water pH of 4.4. The adsorption capacity of nitrate by nano alumina at 25 °C was 4 mg. Also, the presence of anions such as SO₂, Cl and CO₃⁻² has a negative effect on the nitrate removal process. When these anions were present, the nitrate removal efficiency reached 40-45% due to the disproportionate interaction of these anions. Metal alloys such as palladium/silver (PdAg) were fixed on amine (NH₂) on activated SiO₂ levels. The PdAg/SiO₂-NH₂ system was synthesized using formic acid as a reducing agent. The amine factor in SiO₂, formed by the decomposition of

formic acid, improves the nitrate reduction efficiency. Finally, this system showed desirable catalytic properties.

Nitrate removal can also occur through photo catalytic reduction, and semiconductors can act as a suitable catalyst for photo catalytic reduction of nitrate. TiO₂ metal oxide, which is inexpensive and non-toxic and has optical stability, can act as a photo catalyst. TiO₂, NZVI and composites containing TiO₂ and NZVI require UV light to effectively remove nitrate. The components of this type of nano composite, especially NZVI, also have the ability to remove nitrate effectively, but the composite has shown better results and performance. Maximum nitrate removal occurred in a ratio of one to 10 for TiO₂ to NZVI. In another study, carbon-modified titanium electrodes were used as photo catalysts to remove nitrate from seawater. C/TiO₂ nanoparticles were synthesized by sol-gel method using titanium isopropoxide. TiO₂P₂₅ was synthesized using titanium trichloride by a similar method to ensure the absence of carbon in these nanoparticles. In this study, an electron-hole combination was created using formic acid as an electron donor. TiO₂P₂₅ and TiO₂ without surface modification were also compared. In TiO₂ P₂₅ a significant reduction in the optical band gap was observed which led to the removal of nitrate by the photocatalyst under UV light. In the absence of C/TiO₂ nanoparticles, nitrate reduction did not occur, but with increasing catalyst concentration, the reduction process efficiency also increased. The pH of the solution also played an important role in the nitrate reduction process. At low pH, a sharp increase in the nitrate reduction process was observed, while at high pH, the decrease in nitrate was relatively less due to the lack of absorption due to electrostatic repulsion. The concentration of formic acid plays an important role in the process of reducing nitrate and with increasing the concentration of nitrate, the rate of nitrate reduction process also increases significantly. However, this increase in the reduction process has only a saturation point and a uniform limit. In general, the maximum removal of nitrate was observed when the amount of catalyst was 0.5 g/l and the pH of the solution was 3 and the concentration of formic acid was 0.04 mg. Nanoparticles, especially when used as a reducing agent to remove nitrate, produce ammonia as a main product. Ammonia is toxic and its production is not desirable. Therefore, it is necessary to optimize the nanoparticles to produce non-toxic nitrite, ammonium and nitrogen gas. Nanoparticles can be designed to remove nitrate-containing contaminants simultaneously. The presence or absence of these common contaminants also significantly affects the efficiency of nitrate removal.

Carbon nanotubes (CNTs) have been widely used in water treatment due to their variable chemical, physical, electrical and structural properties. They can be used as adsorbents, catalysts and catalyst aids to remove contaminants. Carbon nanotubes have been used as adsorbents to remove dyes, heavy metals and other types of organic and inorganic contaminants due to their high adsorption rate and optimal efficiency. However, the surface of carbon nanotubes is very hydrophilic and needs surface correction. Modifying the surface of carbon nanotubes increases the removal efficiency of nitrate. In one study, carbon nanotubes were synthesized using the CVD method and functionalized with ammonia and nitric acid to remove nitrate at room temperature. Nitrate removal efficiency by surface-modified carbon nanotubes was compared with nitrogen groups and carbon nanotubes in oxidized form. Increased nitrate removal efficiency was observed with CNT sheets. The Langmuir isotherm model showed adsorption capacity for nitrate-modified CNT of 142.8750 mg / g and 90.9090 mg / g for oxidized CNT. Modified CNT showed 90% efficiency for nitrate removal in a solution with a concentration of 300 mg/20 ml. Surface-modified nanotubes showed higher nitrate removal efficiency, less equilibrium time and better recovery compared to activated carbon. Magnetic adsorption methods are widely used to remove nitrate from industrial wastewater. Therefore, multi-magnetic wall carbon nanotubes can easily be considered as a high-performance alternative to current systems. The magnetic nature of these nanotubes enables them to be easily separated magnetically, thus preventing further contamination. Magnetic CNTs are synthesized by chemical deposition of Fe₃O₄ on the CNT surface. High mechanical strength, high surface to volume ratio, variety in structure and excellent electrical properties make carbon nanotubes suitable nano materials for nitrate removal.

Nanofibers

Nanofibers are less than 100 nanometers in diameter and are used in various environmental fields. They can be easily fixed on any surface due to their extraordinary length. Also, characteristics such as high surface-to-volume ratio, variety in surface modifications and porosity, are the reason for their use in the filtration of pollutants in the climate. Chitosan is widely used to remove nitrate. In one study, chitosan nanofibers were used to prepare the substrate by electro spinning, and these substrates were used as a stabilizing base to immobilize algal cells. Algal cells are widely used in wastewater treatment because they not only treat water, but also produce algal biomass that can be used to produce biofuels and other applications. Stabilization of algae on the surface allows cells to grow in smaller

volumes and space, allowing for better management and repeated use. Studies on nitrate removal efficiency using stabilized algae on chitosan substrate showed 87% nitrate removal from the effluent (initial nitrate concentration 30 mg / l). Initial removal of nitrate from the effluent was performed by an algae-free nano fiber substrate. In later stages, the concentration of residual nitrate is reduced by algae cells that are constantly growing. In general, nanofiber substrates on which algal cells were stabilized showed equivalent nitrate removal efficiency (87%) compared to nitrate removal efficiency in equivalent cellless substrates (32%).

Nano-powders

Nano shells are usually made of a dielectric core and covered by a thin metal film. In a study conducted by Ensi et al., SiO₂-FeOOH-Fe shell core nano system was used to remove nitrate. SiO₂-FeOOH nuclei were used to stabilize NZVI during the nitrate removal process. When the stabilized NZVI concentration doubled, the nitrate removal efficiency increased from 69% to 86%. Nitrate removal efficiency was lower at lower pH. The contact time in this experiment was 2 hours and sonication for 3 minutes had a positive effect on nitrate removal efficiency. The highest percentage of nitrate removal (99.84%) was observed at a concentration of 64 mg/l at pH 3. Nano clusters are atoms of the same type that are stacked in large numbers next to each other. Nanostructure of iron cluster with high surface to volume ratio is a good option for nitrate removal. In a recent study to remove nitrate, these nano clusters were combined with NZVI. During the synthesis of this type of nano clast, ethanol and water were used as solvents. The synthesized nano clusters were spherical in shape and had a surface area of 54.25 m²g / L and a diameter of 80 nm. The concentration of iron nano clusters plays an important role in reducing nitrate. After increasing the amount of nano clusters, the reaction rate as well as the nitrate removal efficiency increase. However, in an open system, nitrate depletion declined due to the consumption of electrons released from iron nano clusters by dissolved oxygen. Efficient removal of nitrate using nano clusters at pH above 9-10 was considered. OH⁻ production at higher pH caused iron deposition and helped to remove secondary contamination from the water. In addition, the reaction of OH⁻ with other ions in the water reduced the number of other contaminants in the water during the treatment process.

Nanocomposites

Nanocomposites such as polymers, graphene-based nanocomposites, and magnetic polymers have been widely used to purify and remove contaminants.

Nanocomposites contain a combination of nano materials that increase the uptake of nitrate. In a research study, carbon silicon composite in both nano and bulk forms of bamboo was prepared and tested. Bamboo leaves contained silica, so it was chosen as the source. Nitrate adsorption efficiency was measured in nanocomposites (44.98%) and nitrate removal efficiency was observed in bulk composites (21.98%). The preparation method was relatively simple and this technique is also classified as an environmentally friendly process. Studies have been performed on chitosan-based nanocomposites for nitrate removal. Chitosan composites were prepared with polyvinyl alcohol (PVA) and polyethylene glycol (PEG) and used to remove nitrate from water. 0.1 g of the composites were added to the solution containing 10 mg/l of primary nitrate. pH and contact time were 3 minutes and 40 minutes. The amount of nitrate adsorbed for PEG/chitosan was 50.67 mg/g while for PVA/chitosan it was 35 mg/g. Another chitosan-based nano composite was chitosan/zeolite/zirconium oxide nanoparticles (CTS/ZY/Nano ZrO₂) nanocomposites made to remove nitrate from solution by changing the molar ratio of chitosan (CTS) to zeolite/nano zirconium. Nitrate uptake was strongly dependent on the molar ratio of these three CTS nano composite components: Zeolite/nano zirconium, pH and temperature and acidity. This compound absorbed 23.58 m/g nitrate. The highest nitrate removal occurred when the molar ratio of CTS: zeolite/nano zirconium was 5: 1, pH 3, temperature 35 °C and contact time 60 minutes. Chitosan-polystyrene-Zn nano composite is fabricated by loading method to remove nitrate using aqueous solutions. The nanocomposite removed 90% of the nitrate ions from the 25 ml solution, even in small amounts. Initial nitrate and pH concentrations were 3 and 10 mg/L, respectively. These experiments showed a nitrate removal rate of 82.5%. Another nanocomposite, such as chitosan zirconium iron (Fe₃O₄/ZrO₂/CS), has the ability to effectively absorb nitrate from water. Simultaneous adsorption and diffusion of nitrate among ions probably improves the nitrate removal efficiency of 89.3 mg/gr.

Vision of the future

Most studies have been performed on a laboratory scale, so new methods should be developed to facilitate the widespread implementation of this technology and to ensure the efficiency of nitrate removal at the pilot scale. In the future, nano materials can be optimized with nitrate removal techniques. Green synthesis pathways are also among the preferred methods for preparing nano materials. To remove nitrate from the aqueous medium, natural nano materials such as nanoclay can be used. They are very suitable for

environmental applications because they are inexpensive and have a high adsorption capacity with a high level of correction potential. Such properties enable them to be excellent sorbents for nitrates. They can also be used as a stabilizing substrate for various catalysts and thus can improve nitrate removal through reduction processes.

Restriction of Nitrification

In municipal wastewater treatment, in some cases nitrification is limited and, in some cases, it is prevented by the presence of toxic organic and inorganic compounds. A minimum SRT of about 4d is required to achieve complete nitrification at 22-24 °C. An SRT of 12d is required for complete nitrification of municipal wastewater at looc. An SRT of 12d is required for complete nitrification of municipal wastewater at looc. It has been shown that at the looc temperature of the mixed liquid, nitrates are less tolerant than heterotrophic organisms against fluctuations in input composition and temperature for BOD removal and denitrification. The effect of salt content on nitrification was discussed by Hening and Caycer. They found that a concentration of 100 mg/l fluoride reduced the nitrification rate by 80%. Concentrations up to 5 g/L sulfate have no effect. Non-ionized ammonia (NH₃) limits both nitrosamines and nitrobacteria. Because the non-ionized fraction increases with increasing pH, the high pH, along with the high concentration of total ammonia, severely restricts or prevents complete biological nitrification. Because nitrosomonas are less sensitive to the price of ammonia than nitrobacteria, the nitrification process can only be completed in part and lead to nitrite ion accumulation (NO₂-2) because N O₂-2, unlike NO₃-N, is highly toxic to most aquatic organisms. Ammonia toxicity to activated sludge biomass in municipal wastewater treatment is a rare problem. Because the total ammonia concentration is low and the pH of the mixed liquid is almost neutral.

Discontinuous activated sludge nitrification (BAS): In the BAS test method, the wastewater sample is well aerated in the presence of a nitrate-producing sludge. Sludge can be obtained either from municipal activated sludge treatment plant or developed separately from an accessible, economically viable nitrate-producing microbial environment. Regardless of the source of the sludge, it must be possible to determine the mass of nitrates at the concentration of M LVSS because q_N is expressed in units of mass of nitrate makers (VSS_v). The initial concentration of NH₃-N in the BAS test should be 20-50 mg/l to eliminate the induced toxicity of the substrate. If the wastewater contains organic nitrogen, T KN should also be measured to perform biological hydrolysis during the test. Finally, the

alkalinity should be adjusted with sodium bicarbonate (NaHCO₃) to provide 7.15 mg of alkalinity in terms of CaCO₃ mgTKN plus the remaining 50mg/l. A control test should be performed using the same initial N H₃-N concentration. Wastewater sample and control sample should be strongly aerated and sampling should be done over time. The total rate of specific oxidation of NH₃-N is:

$$\frac{38mg/(L.d)}{1200mgVSS/L} = 0.032mg NH_3 - N/(mgMLVSS.d)$$

The specific nitrification rate of nitrates is equal to:

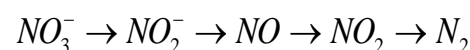
$$q_n = \frac{0.032}{0.0245} = 1.3mgN/(mgVSS_N.d)$$

The specific growth rate of the nitrate makers for a_N=0.15mg/mg was 0.195d⁻¹. Regardless of the effects of temperature, or b_N=0.05d⁻¹, the amount of min (θ_c) is equal to:

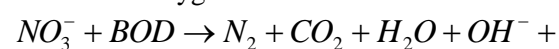
$$(\theta_c)_{min} = \frac{1}{0.195 - 0.05} = 6.9d$$

It should be noted that in the nitrification test BAS, sludge of which its f_N and VSS_N concentration are known is used to determine q_N.

Denitrification: Denitrification or desalination is the second step in nitrogen separation through the desalination process. Separation of nitrogen into nitrate by conversion to nitrogen gas can be made possible under "oxygen-free" conditions, a process called "desalination". Conversion of nitrate nitrogen to an easily separable form can be done by optional heterophobic bacteria. Achromobacter, aerobacter, alcaligenes, bacillus, brevibacterium, flavobacterium, lactobacillus, micrococcus, proteus, pseudomonas, pirillum are among these bacteria. These bacteria can perform nitrate degradation, which is a two-step process. The first step is to convert nitrate to nitrite. After this stage, nitrite oxide, nitrous oxide and nitrogen gas are produced. Nitrate reduction reactions are as follows:



The last three compounds are gas products and can be imported into the air. In nitrification, BOD is used as a carbon source for the center and energy, and nitrate as a source of oxygen.



newcell.

In the denitrification process, about 3.7 g of COD is reduced per NO₃-N g and per gram of reduced NO₃-N, 0.45g VSS, 3.57g alkalinity is produced. This is half

the amount of alkalinity consumed during nitrification. At the same time, part of this alkalinity is eliminated by reacting with the CO_2 produced in microbial respiration. It should be noted here that nitrate-removing bacteria need carbonaceous substances for their activity. And as stated earlier (in previous chapters), carbonaceous substances in wastewater are eliminated in the first stage of oxidation. Therefore, the denitrification operation, should be performed before the first oxidation step, or if the nitrate removal pool is after the first oxidation step, carbonaceous substances such as methanol should be added. The q_{DN} denitrification rate relative to $\text{NO}_3\text{-N}$ concentration is zero and is approximately 1mg N / L and is determined by the following equation:

$$q_{\text{DN}} = \frac{(\text{NO}_3 - \text{N})_o - (\text{NO}_3 - \text{N})_e}{X_{\text{vb}} b}$$

q_{DN} denitrification rate = $\text{gNO}_3\text{-N}/(\text{gVSS}\cdot\text{d})$

X_{vb} = Aerated non-nitrate biomass, mgVSS/L

The denitrification rate for the mixture temperature and dissolved oxygen concentration (DO) is adjusted by the following equation:

$$q_{\text{DN}_T} = q_{\text{DN}_{(20^\circ\text{C})}} \cdot C \cdot \theta_{\text{DN}}^{T-20} (1 - \text{DO})$$

Fixes θ_{DN} range from 1.07 to 1.2.

OH,si|vertin showed that at high levels of dissolved oxygen, the IAWQ equation is more practical:

$$q_{\text{DN}} = q_{\text{DN}(\text{max})} \left(\frac{1}{1 + \text{DO}/k} \right)$$

A recommended value for K is 0.38mg / L . It is assumed that k will be a function of clot size and therefore the amount of energy in the aeration pool. The rate of denitrification, like the aerobic process, depends on the biodegradability of organic materials in the wastewater and the concentration of activated biomass under aeration. This in turn depends on both SRT or F / M and the presence of neutral solids in the sludge. With increasing F/M , the concentration of active biomass and the rate of denitrification increase. Although denitrification can occur under self-devouring conditions (low F/M), using internal biomass storage resources, this is very slow and requires a long retention time (H RT). Since q_{DN} is affected by both wastewater properties and process design parameters, it is usually necessary to determine this rate through laboratory and experimental methods. A discontinuous denitrification test should be

performed in which sludge and wastewater are mixed under anaerobic conditions [(ORP) = -100mV oxidation reduction potential] and residual $\text{NO}_3\text{-N}$ concentration is determined over time. The rate of wastewater denitrification can also be estimated from the rate of oxygen uptake. In this case, the wastewater anaerobic sludge mixture is aerated and the SOUR is determined over time. The correlation between the R_{DN} and SOUR shows that 1mg of $\text{NO}_3\text{-N}$ is approximately equivalent to 3mg of O_2 , which is in good agreement with the theoretical value.

In cases where a carbon source is not available in the wastewater, methanol can be used as a carbon source. Denitrification in final clarifiers causes sludge to float and increase suspended solids to be released. Nitrogen gas production rate depends on the carbon source available for denitrification, SRT , temperature and sludge concentration. Henze et al. [9.] estimated that $6\text{-}8$ and $8\text{-}10\text{mg / l}$ of $\text{NO}_3\text{-N}$ is needed to be de-nitrated in the sludge bed to cause the sludge to float at 10 and 20°C , respectively. Most of the denitrification is absorbed as a result of respiratory self-devouring and consumption of slowly degradable organic material. This in turn is related to the active mass, which is a function of S RT .

Conclusion

In order to remove nitrogen biologically from wastewater (sewage), the system should be directed to the salinization and desalination processes. There are several systems and processes for achieving the nitrification and denitrification, so in municipal wastewater treatment plants, to complete the municipal wastewater treatment operation, sectors are considered whose purpose is to separate nitrogen from wastewater and extraction of nitrogen gas using these biological processes. All the biological processes of nitrogen removal in municipal wastewater treatment plants have an aerobic zone (1) in which biological nitrification takes place. Important operational parameters (for nitrification) are: pH , dissolved oxygen, aeration periods, mean cell retention time and carbon to nitrogen ratios and temperature are effective factors for all of these variables. At higher temperatures, carbon oxidation is possible in conjunction with nitrification; but for colder wastewater, in most cases, separate systems are required. Depending on the total nitrogen removal in the wastewater, denitrification (nitrogen removal) by $\text{NH}_4\text{-N}$ oxidation and $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$ reduction to nitrogen gas is conducted to complete denitrification. In general, all the biological nitrogen removal systems in municipal wastewater treatment plants are different combinations and forms of aerobic-anaerobic sequences.

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