Evaluation of the performance of different nitrate removal methods from groundwater

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ABSTRACT

Pollution in any form has always been a concern for humans. If the pollution occurs in an inseparable part of his life this will lead to generational crises. On the other hand, measuring groundwater contamination levels or distinguishing contamination is naturally more difficult compared to other water resources. One of the most crucial and abundant form of water contamination is nitrate which is an ion of oxygen and nitrogen that mostly is added to soil through agricultural applications. This causes massive health issues for any living creatures. Water treatment has been applied for years and our ancestors had their own traditional ways for this. Nowadays, depending on the type of contamination, there are various water treatment options as well. Removal methods include on-site and off-site treatment, biological and physiological process. Carbon appears to be a suitable solution for this issue that can be added to water in different ways. In this essay, a narrative review provided on all the nitrate removal methods ranging from direct to indirect methods. Additionally, influential environment factors such as dissolved oxygen pH, temperature, mineral materials, encounter time, adsorption capacity are discussed. Finally, biological heterotroph has introduced as the efficient solution while surface adsorption has considered as the most economical solution.

Keywords: *water contamination, groundwater, Nitrate removal, groundwater contamination, activate carbon, surface adsorption, autotroph heterotroph, ion exchange*

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1. *INTRODUCTION*

Nitrate contamination mainly occurs by human interference in agriculture and has recently exceeded the safety level. Environmental protection agency (EPA) in 1990 indicated that 250,000 water supply sources had maximum contaminant levels (MCL) for nitrate. The World Health Organization (WHO), 2004 found that 30% of the 2,000 sources surveyed in world had more than 24 mg /L. [1] Nitrate can enter groundwater either naturally or synthetically and it may be concentrated in specific areas or spread over a wide region. Natural sources of nitrate in groundwater are continuous mineral interactions within an aquifer, bacterial activity and the presence of algae in fissures whether water is still or moving. In arid or semi-arid areas where there is no human agricultural activity, anthills, termite mounds and biological soil crusts are the most significant sources of nitrate contamination. Although nitrate contamination by human interference mainly occurs by over fertilizer utilization in high dosages, other factors such as fertilizer pond, industrial discharge, septic systems or leaky sewage, urban forest contribute in ubiquities challenge. The presence of high dosage of nitrate in drinking water causes non-hodgkin lymphoma, different type of cancers and poor thyroid function in adults and diabetes in children, potential cause of neural congenital diseases and Methemoglobinemia in under six months toddlers. [2] Here, we discuss the negative effects of nitrate on groundwater, the mechanism of groundwater contamination by nitrate and different methods for its mitigation.

1.1 Natural nitrate removal from groundwater

Nitrate removal process is similar to nitrate pollution process which occurs by natural or Synthetic phenomenon. When the root of plants absorbs the necessary nitrogen and transform this nitrogen to desirable form means nitrate and this natural process calls nitrification. Nitrate reduction may occur by plant uptake, mineralization-immobilization processes, volatilization, and losses by run-off and denitrification. [3]. Nitrate ions are loosely bound and are more likely to penetrate into the phreatic zone of a groundwater aquifer.[3] Usually nitrate reduction policies implemented in areas with over 60% nitrate polluted where no oxygen left for microbes to consume. [3]

Nitrate reduction by microbes is a respiratory process in which nitrate or nitrite serves as the final electron acceptor in the absence of oxygen. As a result of this adenosine triphosphate reaction, a high-energy molecule is produced and electrons transfer the released energy to denitrifying bacteria in order to synthesize new biological mass.[3] Although this process is generally effective in reducing naturally occurring nitrate, the annual input of approximately 70 kg of nitrate per hectare into the soil due to agricultural practices in Iran necessitates reinforcing natural nitrate reduction with synthetic methods.

1.2 Synthetic nitrate removal from groundwater

The aim of synthetic nitrate removal is not to completely eliminate nitrate from groundwater, but rather to reduce its concentration to 50 mg/L, which is the safe level recommended by the WHO. A daily intake of less than 3.7 mg of nitrate by adults is considered harmless. However, higher intake may lead to the aforementioned health problems. Nitrate removal can occur through either biological or physicochemical methods.

In the biological method, certain types of nitrate-consuming bacteria or microbes are utilized. On the other hand, physicochemical reduction begins when polluted water comes into contact with specific metals or catalytic elements. In biological method, nitrate-consuming bacteria grows whether heterotrophically or autotrophically. The result of experiments on two type of bacteria is showed in table. Based on the result, autotrophic bacteria functions better in nitrate reduction.

Table 1. A comparison between autotroph and heterotroph bacteria in nitrate removal function

Nitrate Removal Method	***Nitrate Removal Percentage***	***Electron donor***	***Hydraulic contact time***	***Inlet concentration (mg/lit)***	***pH***	***Temperature***	***References***
Autotroph	*100%*	*granulated sponge iron, zero-valent iron (ZVI), and pine bark*	*16 days*	*103.9*	*7.3-8.3*	*15-33*	*[4]*
Autotroph	*95%*	*Iron (II)*	*12 hours*	*50*	*6*		*[5]*
Autotroph	*>90%*	*Pyrite*	*6 days*	*56.69*	*6.5-6.7*		*[6]*
Autotroph	*98-64%*	*Sodium thiosulfate*	*2-24 hours*	*150*	*7.4*	*25*	*[7]*
Heterotroph	*-*	*sucrose, ethanol, methanol*	*31 hours*	*50-70*	*7.0-7.5*	*15-20*	*[8]*
Heterotroph	*100*	*Ethanol*	*-*	*417.1*			*[9]*

Heterotroph	*80*	*Glucose syrup*	*400*	*[10]*
Heterotroph	*97-95*	*Ethanol*	*240-1300*	*[11]*

Carbon is used in both biological methods. Complex carbon compounds are used in the heterotrophic method, and inorganic carbon compounds are used in the autotrophic method. The transformation of nitrate to nitrogen gas involves four steps. First, nitrate (NO_3^-) is converted into nitrite (NO_2^-) by microorganisms. Next, the nitrite ion is converted into NO, then into nitrogen oxide (N_2O), and finally into nitrogen gas. [12] However, in the physicochemical method, carbon can also be used as an adsorbent when in contact with polluted water. This is a physical reaction, and only superficial absorption occurs during the process. Nitrate reduction happens through ion exchange, membrane bioreactors, or biofilm-electrode reactors. Other methods, such as chemical reactions by metals, reverse osmosis, nanofiltration denitrification, and catalyst denitrification, reduce nitrate without direct contact with the nitrate, which is not studied in this article.

1.3.1 Biological nitrate removal by heterotrophic bacteria

Complex organic compounds used for heterotrophic energy source and degradable substrates includes methane, methanol, ethanol and carbon monoxide and acetic acid 52-48 has mentioned and related equations has shown.[1] Heterotrophic denitrification automatically occurs in areas where bacteria and mentioned nitrate compounds are available and if these compounds parse the process begins. However, the process slowly happens and only small amount of nitrate filters.

The amount of filtered nitrate highly depends on the quality of the absorbent. Hence, in some cases, additional carbon is added to groundwater to increase the rate and amount of denitrification.[3] Usually, low-molecular-weight carbon compounds such as acetate are added to contaminated water in liquid, solid, or gaseous forms. Typically, the by-products produced act as carbon absorbents and also increase the rate of denitrification. This method has some disadvantages, such as being costly, altering the chemical structure of the soil, and causing regional space limitations. However, these disadvantages are often associated with the use of liquid forms of carbon absorbents.[3]

***Table 2**. Equations of denitrification reactions by heterotrophic bacteria using different carbon sources*

Equation number	***Sub-layer***	***Stoichiometric equation***
1	*Ethanol*	$5\ C_2H_5OH + 12\ NO_3^- \rightarrow 10\ HCO_3^- + 2\ OH^- + 9\ H_2O + 6\ N_2$
		$0.613\ C_2H_5OH + NO_2^- \rightarrow 0.102\ C_5H_7NO_2 + 0.714\ CO_2 + 0.286\ OH^- + 0.980\ H_2O + 0.449\ N_2$
		$5\ CH_3COOH + 8\ NO_3^- \rightarrow 8\ HCO_3^- + 2\ CO_2 + 6\ H_2O + N_2$
2	*Acetic acid*	$0.819\ CH_3COOH + NO_3^- \rightarrow 0.068\ C_5H7NO_2 + HCO_3^- + 0.301\ CO_2 + 0.902\ H_2O + 0.466\ N_2$
3	*Propanol*	$0.278\ C_3H_7OH + NO_3^- \rightarrow 0.5\ N_2 + 0.833\ CO_2 + 0.611\ H_2O + N_2$
4	*Cellulose*	$5(C_6H_{10}O_5)_n + 24n\ NO_3^- \rightarrow 6n\ CO_2 + 13n\ H_2O + 12n\ N_2 + 24n\ HCO_3^-$
5	*Butanol*	$0.208\ C_4H_9OH + NO_3^- \rightarrow 0.5\ N_2 + 0.833\ CO_2 + 0.542\ H_2O + OH^-$
6	*Aromatic Hydroxypropyl*	$C_{61}H_{67} + 62.2\ H^+ + 62.2\ NO_3^- \rightarrow 31.1\ N_2 + 61\ CO_2 + 64.6\ H_2O$
7	*Organic matter*	$C_5H_9NO + 3.36\ NO_3^- + 3.92\ H^+ \rightarrow 1.68\ N_2 + 0.36\ C_5H_7NO_2 + 3.2\ CO_2 + 3.92\ H_2O + 0.64\ NH_4^+$
8	*Methan*	$5CH_4 + 8NO_3^- + 8H^+ \rightarrow 4N_2 + 5CO_2 + 14H_2O$
9	*Glucose*	$C_6H_{12}O_6 + 2.8\ NO_3^- + 0.5\ NH_4^+ + 2.3\ H^+ \rightarrow 0.5\ C_5H_7NO_2 + 1.4\ N_2 + 3.5\ CO_2 + 6.4\ H_2O$

Limitations associated with heterotrophic denitrification include low substrate or bed distribution rates, alginate complex reaction products, and short alginate lifespan.[1] To address this issue, a membrane-stabilized biofilm reactor was developed in laboratory research, where denitrifying bacteria and a carbon energy source were separated from the water being treated.

However, replicating this method on a practical scale would be both costly and impractical. Research is also progressing toward the development of slow-release polymers or carbon-based materials capable of sustaining denitrification at a constant rate over an extended period. Table 3 summarizes the findings of studies on heterotrophic bacteria and the various denitrification methods involving them.

***Table 3**. Summary of experiments performed by heterotrophic bacteria*

References	***Method***	***Absorbent***	***Temperature (Centigrade)***	***Nitrate Concentration (mg/L)***	***C/N Ratio***	***Nitrate Removal Rate***
[13]	*Biological sand filters*	*Ethanol*	۲۹	*110.7*	*1.1-1.8*	*44%-53%*
[14]	*Biological nitrate removal*	*Ethanol*	*25*	*200*	*5*	*100%*
[14]	*Biological nitrate removal*	*Methanol*	*25*	*200*	*5*	*99%*
[15]	*Biodegradable polymer*	*3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV) and polylactic acid (PLA)*	*-*	*-*	*-*	*0.31 mg/h*
[16]	*Biological denitrification using an oxygen-free rotating biological contactor*		*-*	*100*	*1.25*	*97%*
-	*Packed bed bioreactor*		۲۹-۲۰	*-*	*1.82-3.73*	*88%-97%*

1.3.2 Biological nitrate reduction method using autotrophic bacteria

Autotrophic denitrification is carried out by nitrate-consuming bacteria such as Ferrobacillus, Gallinula, Leptothrix, Sphaerotilus, Paracoccus, Thiobacillus, and Thiosphaera.[3] Carbon, in the form of carbon dioxide or bicarbonate, is used both for microbial cell synthesis and as an electron donor in this denitrification method. This method is slower than other denitrification methods and produces less biomass. Autotrophic denitrification can be carried out by bacteria such as Ferro bacillus, Leptothrix, and Sphaerotilus, which obtain energy from ferrous iron (Fe^{2+}) as an electron donor. Other bacteria such as Paracoccus, Thiobacillus, and Thiosphaera use reduced sulfur compounds (e.g., S^0, S^{2-}, $S_2O_3^{2-}$, $S_4O_6^{2-}$, SO_3^{2-}) as electron donors to drive the process.[3] If carbon dioxide is used as an electron donor in the reaction, the corresponding reaction equation is as follows:

$H_2 + 0.35\ NO_3^- + 0.35\ H^+ 0.052\ CO_2 \rightarrow 0.010\ C_5H_7O_2N + 0.17\ N_2 + 1.1\ H_2O$

Experiments on this reaction have shown that the efficiency of denitrification can also be influenced by pH. [3] reported an optimal nitrate removal of 95% using Fe^{2+} *as the electron donor, with an influent nitrate concentration of 50 mg/L, a hydraulic retention time (HRT) of 12 hours, and a pH of 6.0.[3] In a study by Sotoodehnia et al. (2024), autotrophic denitrification using oxidized and non-oxidized pyrite extracted from four mines in Iran—including the Sangan Iron Mine, Miduk Copper Mine, Smulan Iron Mine, and Sungun Copper Mine—was investigated. The results indicated that oxidized pyrite from the Sungun Mine achieved a 15% nitrate removal rate, while non-oxidized pyrite from the Miduk Mine removed only 53% of nitrate. Although autotrophic denitrifiers significantly less nitrate compared heterotroph method, the standardized cost of heterotrophic nitrifiers such as ethanol per NO3 removal value is still higher than autotrophic denitrification such as pyrite, which makes the use of autotrophic nitrifiers still more demanding. [14] This cost-value aspect should be considered in addition to the environmental effect of autotrophic nitrifiers when selecting autotrophic and heterotrophic denitrifies.[14]*

1.3.3 The effect of various factors on the biological denitrification process

1.3.3.1 Dissolved oxygen

Biological denitrification has been reported to occur under anaerobic or anoxic conditions (Eh values ranging from −144 to +6.8 mV) at a depth of 140 meters in groundwater.[3] Denitrification is carried out by denitrifying bacteria under anoxic or anaerobic conditions, typically at dissolved oxygen (DO) levels below 0.2 mg/L. [3] Fortunately, anoxic conditions required for denitrification are present in many aquifers. However, the presence of dissolved oxygen (DO) can inhibit the activity of key enzymes involved in denitrification, such as nitrate reductase and nitric oxide reductase. As a result, the reduction process may be incomplete, leading to the accumulation of toxic intermediates such as nitrite instead of molecular nitrogen (N_2)*. [3]*

1.3.3.2 Temperature

The growth rate of nitrogen-fixing bacteria is linked to increasing temperature. [4] In a 2008 study, Rivett et al. reported that denitrification typically occurs within a temperature range of 2–35 °C, with optimal activity observed between 25 and 30 °C. However, the increase in the reaction rate also depends on the type of available carbon source, with the highest growth rates observed when methanol or acetic acid is used. According to Gilbert et al. (2008) and Liu et al. (2013), the optimum temperature for denitrification ranges between 25 and 35 °C. Fugalar et al. 2004 showed the relationship between temperature and denitrification using the Arrhenius equation.

$$K = A \times e^{((-EA)/(R\times T))} \tag{3}$$

where k is the reaction rate (mg/L·h), A is the frequency factor, Ea is the activation energy (kJ/mol), R is the universal gas constant (kJ/mol·K), and T is the absolute temperature (K).[3] Typically, low temperatures extend the adaptation period of denitrifying bacteria. [21] Groundwater temperature typically varies with depth, geological conditions, and geographic location. [3] Shallow groundwater is affected by surface temperatures, which makes it warmer compared to water in deeper areas of the same aquifer.[3] Hiscock et al. (1991) reported that the rate of denitrification decreases at low temperatures, between 0 and 5°C.

1.3.3.3 pH

Biological denitrification is difficult or even stopped in acidic environments and, in general, this reaction, like the adsorption reaction, is sensitive to pH. The best pHfor biological denitrification reactions is between

5.5 and 8. [17][22] Heterotrophic denitrification is an alkaline process that brings the final reaction to a near-neutral pH.. [3]

1.3.3.4 Mineral compounds

The presence of toxic mineral compounds in groundwater has been shown to inhibit groundwater denitrification. [3] In 2017, Gee et al. conducted a study on the effects of heavy metals—including Cd (II), Cu (II), Ni (II), and Zn (II)—on aerobic nitrification. The results indicated that the degree of nitrification inhibition by these metals followed the order: Cd (II) > Cu (II) > Ni (II) > Zn (II). [3] In another study by Kiskira et al, the effect of other metals such as copper, nickel, and zinc showed that adding these metals at initial concentrations of 5, 10, 20, and 40 mg / L resulted in a reduction in denitrification to about 6, 8, and 6 percent, respectively. The severity of inhibition caused by toxic inorganic contaminants in groundwater depends on the type and concentration of mineral contaminants present in the groundwater. [3]

1.3 Membrane bioreactors

In the membrane bioreactor (MBR) method, contaminated groundwater is passed through a microporous membrane, where it undergoes purification and denitrification. The denitrification process takes place in the membrane shell, as nitrate ions diffuse through the micropores.[3] In this method, ethanol is commonly used as a carbon source. To enhance the efficiency of membrane bioreactors, additional treatment methods—such as ion exchange and biological processes—are often employed.

In one study, an anoxic MBR–aerobic biological bioreactor equipped with a submerged microfiltration (MF) membrane was designed and constructed for the removal of nitrate from drinking water. Its performance was evaluated over a 34-day period for the removal of nitrate, nitrite, and turbidity.

The experimental results showed that the nitrate removal efficiency ranged from 14% to 71%, depending on the stability of the operating conditions in the anoxic bioreactor. Moreover, the effluent nitrate concentration from the anoxic bioreactor consistently remained below the permissible limit set by the WHO. [23] The results show that this method has high performance in nitrate removal.

1.5 Nitrate reduction method using carbon adsorption (physicochemical methods)

This is a physicochemical method that does not rely on bacteria or microorganisms for the denitrification process. Instead, denitrification is achieved with relatively high efficiency using a carbon-based nitrate adsorbent. Compared to other methods, this approach is more cost-effective and does not produce by-products through complex reactions, nor does it require additional treatment of the resulting effluent. It is more accessible, widely applicable, and requires less energy to carry out the reaction.

This reaction requires only a carbon-based adsorbent and nitrate-contaminated water. However, several environmental factors can influence the denitrification rate and overall efficiency of the process, including PH, contact time with the adsorbent, initial nitrate concentration, adsorbent surface area and dosage, temperature, degree of adsorbent activation, and the presence of active ions essential for the reaction.

1.5.1 Adsorbent

Various organic industrial wastes such as fly ash, red mud, slag, bamboo powder, chitosan, mesoporous silica, cement paste, and nano-alumina are commonly used as adsorbents. In addition, natural materials like clay, zeolite, and sepiolite have also been widely applied for this purpose. In a 2015 study, Mohammad Hassan Shah Moradi investigated four adsorbents for nitrate removal: rice bran, sludge from the primary settling pond of a wood and paper mill wastewater treatment facility in Guilan Province, conventional commercial activated carbon, and coal.

The rice bran and activated sludge adsorbents were first dried, sieved, and ground into powder. Following $ZnCl_2$ activation, they were dried again, their pH was stabilized, and then subjected to a final drying step. The other adsorbents underwent a similar preparation process, except that their pH was stabilized immediately after the powdering stage.

1.5.2 Contact time

The time required for maximum nitrate absorption by the adsorbent will be the contact time. The contact time can vary from one hour to 120 hours for different adsorbents (input concentrations vary). If the contact or mixing time is sufficient, the adsorption rate increases, and diffusion into the pores occurs efficiently. However, if turbulence between the adsorbent and the fluid is low, the adsorption process may be hindered due to the development of a thicker stagnant liquid layer around the particles, which limits mass transfer.[25]

1.5.3 pH

Given that the nitrate ion has a negative charge, the adsorption rate increases at acidic pHs due to the electrostatic interaction that occurs between the positive surface charge and the anions, but at higher pHs the adsorption rate is lower. [26] Of course, the difference in adsorption rate between acidic and alkaline pH conditions is relatively small. Considering the initial nitrate concentration and the required removal amount to reach the standard level, it is possible to achieve the desired result at the natural pH of the water with minimal energy expenditure. [26]

1.5.4 Carbon activation

Carbon activation involves contacting it with a salt that significantly enhances the adsorption capacity. In fact, surface modification of the adsorbents is necessary to improve adsorption. This salt is commonly $ZnCl_2$. It is important to note that the increase in adsorption when the adsorbent is activated with $ZnCl_2$ is due to the creation of additional micro pores.[26] Furthermore, upon activation, $ZnCl_2$ itself acts as an adsorbent in the mesoporous pores and aids in the nitrate adsorption process.[26] Considering the use of $ZnCl_2$ to enhance the nitrate adsorption capacity of the adsorbents, it is important to examine the zinc concentration in the final samples. According to Iranian standards, the permissible concentration of zinc in drinking water is 3 ppm.[26]

1.5.5 Adsorbent concentration value

Increasing the adsorbent concentration can enhance the surface area and the number of active sites available for ion adsorption. Therefore, by increasing the amount of adsorbent, the total surface area and, consequently, the adsorption capacity are also increased. [26] Obviously, increasing the concentration of the adsorbent has a limit, because the concentration of nitrate in water is limited. [26] Table 4 presents the results of research on various adsorbents, including Mohammad Hassan Shah Miran's study on the four mentioned adsorbents, as well as other studies and their findings.

Table 4. Summary of experiments conducted using the surface adsorption method

References	***Absorbent***	***Absorbed Amount (mg/g)***	***Input Concentration (mg/l)***	***Contact Time (hours)***	***Temperature (Centigrade)***	***pH***
[27]	*Zncl2 GAC coconut shell*	*10.2*	*5-200*	*2*	*25*	*5.5*

[27]	*GAC unrefined coconut*	١.٢	*5-200*	*2*	*25*	*5.5*
[28]	*sugarcane pomace*	*87.42*	*1-30*	*48*	*30*	*-*
[29]	*Ammonium-functionalized mesostructured silica*	*46.6*	*100-700*	*1*	*5*	*<8*
[30]	*Chitosan beads*	*90.7*	*25-1000*	*24*	*30*	*5*
[31]	*Sepiolite activated by HCl*	*38.16*	*100*	*5*	*-*	*-*
[32]	*Powdered activated carbon*	*620*	*-*	*1*	*25*	*<5*
[25]	*Rice bran activated carbon*	*80.9*	*75*	*4*	*28*	*4*
[25]	*Activated carbon sludge paper industry*	*74.5*	*75*	*4*	*28*	*4*
[25]	*Commercial activated carbon*	*68.9*	*75*	*4*	*28*	*4*
[25]	*Commercial activated carbon*	*42.1*	*75*	*4*	*28*	*4*

1.6 Ion exchange

The ion exchange process is carried out by passing nitrate-contaminated water through a layer of resin containing anions with high exchange capacity, in which nitrate ions are exchanged for chloride or bicarbonate until the resin is exhausted.[1] A comparison of the use of trimethylamine resins in ion exchange showed that bicarbonate had the highest exchange capacity, followed by chloride, nitrate, and phosphate resins in the comparison.[3] These resins are specially designed to have a large number of carbon atoms surrounding the ammonium nitrogen functional groups to increase nitrate selectivity.[3]

In an experiment, the ion exchange process was tested for nitrate removal from groundwater containing 16-23 mg/L of nitrate, with a flow rate of 31.5 L/s.[34] Triethylamine resins showed a 62% increase in bed life when treating water containing 5.1 meq/L of nitrate and 5.6 meq/L of sulfate.[1] The use of reductant was reduced by 25 to 50 percent, thus reducing the operating cost of the ion exchange process.[1] Although carbon is not used directly in this method, it remains economical and effective in nitrate removal. The ability to regenerate spent resins for reuse makes it an economically viable option for water purification.[3]

1.7 Electrocatalytic method

In this method, water contaminated with nitrate is purified using carbon fibers and applying an electric current. In an experiment, three carbon fibers with a 30% Rh (rhodium) coating of one microgram cm were used at an applied potential of 1.5 volts against a standard calomel (mercury chloride) electrode (SCE) with a platinum secondary electrode.[1]

The results showed a reduction of nitrate from 73 to 39 mg/L within a time interval of 40 to 60 minutes. This method, which uses electric current for direct nitrate removal, achieved an efficiency of 46%. Compared to the absorption method, it can be concluded that this method is more expensive due to the application of electric current and has lower efficiency.

1.8 In-situ nitrate removal from groundwater using the pump and filter method

In-situ methods can reduce the costs associated with pumping, treatment, and reinjection. In-situ treatment is carried out by isolating pollutant masses and applying treatment systems that perform denitrification within the subsurface. [3] In this method, carbon is used as an electron donor, similar to the biological denitrification process. The efficiency of the process is influenced by several factors, including the separation of the contaminated flow mass, the accuracy of predicting the heterogeneous properties and flow parameters in the subsurface, and the adequate accessibility of the reactive zone in contact with the contaminant mass.

Schipper et al. (۲۰۱۰) demonstrated that nitrifying bioreactors can be effectively used to remove nitrate, pathogens, and pharmaceutical compounds from groundwater. In their study, solid carbon substrates were employed for the treatment of nitrate-contaminated groundwater. However, similar studies have raised concerns regarding contaminant migration and the long-term effectiveness of permeable reactive barriers (PRBs) used as nitrifying systems.

In future research, this problem can be solved or countered by using multi-barrier systems and permeable reactive barriers.[3] The efficiency of nitrate removal in this process is influenced by factors such as particle size, surface area, and surface chemistry.

For in situ groundwater denitrification, carbon-based electron donors should be capable of supporting long-term denitrification without introducing limiting conditions. Ideally, organic carbon sources used as electron donors should exhibit moderate reactivity, ensure sustained denitrification over time, be cost-effective, readily available, and easy to handle.[3]

1.9 conclusion

Our country currently has a water resource deficit of about seven billion cubic meters annually. Given that rainfall and resource inputs are almost constant, the only way forward to balance consumption and inputs is through optimal consumption and reuse of used water. Proper treatment and reuse of wastewater can play a significant role in groundwater management and the conservation of water resources.

In this article, both direct and indirect carbon addition methods for groundwater denitrification have been reviewed. If we were to examine these methods in terms of efficiency in their best tested state, they would be, respectively, heterotrophic biological denitrification, autotrophic biological denitrification, surface adsorption physicochemical denitrification using carbon, membrane bioreactor biological denitrification, ion exchange physicochemical denitrification, and electrocatalytic physicochemical denitrification.

Moreover, in terms of cost-effectiveness, accessibility, and ease of implementation, the surface adsorption method using carbon stands out as the most favorable option, primarily due to its minimal equipment requirements and the potential use of industrial waste materials as adsorbents. In some of the aforementioned methods, the addition of carbon may necessitate secondary treatment. Table 5, compiled by Ghanbari Adivi et al. (2010), presents the advantages and disadvantages of selected denitrification methods discussed in this article.

Table 5. Examining the advantages and disadvantages of each of the mentioned methods

Process	***Advantage***	***Disadvantage***	***References***
Biological Method	*Achieving efficiency of over 99%, environmental friendliness, moderate*	*Factors such as the need for waste disposal, the significance of temperature*	*[12]*

	operating cost	*effects, and the necessity for final treatment due to the presence of microorganisms must also be considered when evaluating denitrification methods.*	
Surface absorption	*No need for final treatment, suitable efficiency using the type of adsorbent, ease of operation, moderate operating cost*	*The need to dispose of saturated absorbents, the importance of the effect of pH and temperature*	*[36]*
Ion exchange	*Irrelevant pH and temperature effects, achieving efficiencies of over %, flexibility with pressure changes, moderate operating cost*	*The need to dispose of production wastewater, the need for final treatment due to the corrosiveness of the produced water, filling the resin capacity in the presence of organic materials, operational problems with resin regeneration*	*[37]*

As mentioned earlier, the surface adsorption method is considered the most favorable in terms of ease of use, accessibility, and minimal secondary pollution. However, it faces certain limitations, particularly related to temperature and PH sensitivity, which can hinder its effectiveness. Ongoing research aims to develop purification methods with fewer limitations, higher efficiency, and improved cost-effectiveness. It is hoped that future advancements will lead to the realization of such optimized techniques.

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