Nitrate removal from groundwater: a review of natural and engineered processes
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ABSTRACT
Nitrate contamination of groundwater is a global issue that has stimulated significant research interest. Understanding the prevailing processes of nitrate removal from groundwater, influences of process conditions and the performance of various approaches are vital for successfully dealing with nitrate remediation. Natural and engineered processes of nitrate removal from groundwater are discussed with focus on the performance of natural and engineered innovative techniques for nitrate removal from groundwater. Nitrate removal from groundwater can be accomplished through microbial autotrophic and heterotrophic mechanisms in the subsurface under natural and engineered conditions. The application of these processes to in-situ and ex-situ nitrate removal is also discussed in this review. Further, the effect of temperature, pH, electron donor and biogeochemistry on groundwater nitrate removal are elaborated. While natural attenuation processes result in small amounts of nitrate removal from groundwater, engineered processes are able to achieve significantly higher nitrate removal from groundwater. However, the challenges of secondary pollution need to be addressed in adopting these technologies for groundwater treatment for potable use.
Key words | adsorption, denitrification, groundwater pollution, nitrate, permeable reactive barrier (PRB), remediation

INTRODUCTION
The use of groundwater resources is increasingly becoming prominent in both developing and developed nations. Groundwater represents the world’s largest volume of unfrozen freshwater resource (Margat & van der Gun 2013; Karan et al. 2014; Smith et al. 2016). The importance of groundwater for mankind is underscored by the increasing global application of groundwater (>986 km³/year) for irrigation, industrial use and for drinking purposes, amongst others (Margat & van der Gun 2013; Zhou et al. 2015). Though located in the subsurface, groundwater can become contaminated and unsafe for human use. Nitrate contamination of groundwater is a global problem which requires technological and policy interventions to mitigate its impacts on humans and the environment. High nitrate concentrations in groundwater have been recorded in many parts of the world. Thus, recent research efforts have been focused on understanding the pathways of nitrate generation and contamination in groundwater as well as the development of environmentally friendly nitrate treatment and removal options from groundwater.
Nitrate is a stable and chemically unreactive species of nitrogen which occurs as a part of the nitrogen cycle. Nitrate (NO₃⁻) is the most oxidized form of combined nitrogen for oxygenated systems (Equations (1) and (2)). However,
Nitrate can be reduced by microbial and chemical processes to nitrite, ammonia and nitrous oxides, and nitrogen gas under different environmental settings (Equation (3)):

\[
4 \text{NH}_4 + 7 \text{O}_2 \rightarrow 4 \text{NO}_2 + 4 \text{H}^+ + 6 \text{H}_2\text{O} \quad (1)
\]

\[
2 \text{NO}_2^- + \text{O}_2 \rightarrow 2 \text{NO}_3^- \quad (2)
\]

\[
\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2 \quad (3)
\]

Nitrate concentrations in groundwater are controlled by biogeochemical processes and can be location specific. Thus, nitrate concentrations in groundwater may vary spatially and temporally (Rivett et al. 2008; Arslan et al. 2017). Groundwater contamination by nitrate may result from anthropogenic and geogenic influences that may be from either diffused or point sources. Geogenic nitrate contamination of groundwater may result from the continuous interaction between the minerals of an aquifer media, bacteria and algae found in cracks and fissures of geologic formations where groundwater flows or is stored (Obiri-Nyarko 2012). Besides, in aquifer storage and recovery (ASR), microbial clogging following injection has been reported as a major issue, and this problem should be considered during the selection of aquifers for groundwater recharge (Smith et al. 2013).

The use of high doses of fertilizers in intensive agriculture practices has been identified by many studies as a significant contributor to groundwater nitrate pollution (Nas & Berktay 2006; Sacchi et al. 2013). However, other significant sources of nitrate pollution of groundwater include: manure pools, industrial discharges, leaky septic and sewer systems, urban forest and grasslands, and river and aquifer interactions (Groffman 2000; Bhatnagar & Sillanpää 2011; Archna et al. 2012; Haller et al. 2013; Omer & Alzahrane 2013; Zhou et al. 2015). In arid and semi-arid areas where there are limited or no agricultural activities, ant hills, termite mounds and biological soil crusts have been reported as major contributing sources of nitrate contamination into groundwater (Stone & Edmunds 2014).

The World Health Organization (WHO) has set drinking water standards for nitrate as 50 mg/L (WHO 2011). One of the notable health impact of long-term ingestion of water with elevated nitrate concentrations (i.e. >50 mg/L) is methemoglobinemia, which is popularly called the ‘blue baby syndrome’ in infants below six months (Lorna 2014).

With the increased consumption of groundwater globally, there is therefore the need for innovation of technically and economically feasible, scalable and efficient alternatives for treating nitrate in groundwater.

The dynamics of nitrate pollution of groundwater and its attenuation in the subsurface porous unconfined/confined rocks is governed by complex biogeochemical processes (Bourke et al. 2018). Besides being influenced by recharge conditions, groundwater chemistry may be impacted by the mineral kinetics of water–rock interactions (Brantley et al. 2008; Yidana et al. 2012). As a result, requirements for the selection of appropriate nitrate removal technologies can be daunting. A summary of the characteristics, performances and applications of nitrate removal and reduction methods are presented in this review. The review aims to critically describe different groundwater nitrate removal techniques, their performances and process conditions, and identify further research needs.

King et al. (2012) classified the treatment technologies in two categories, i.e. nitrate reduction and nitrate removal options. Nitrate removal technologies involve physical processes that does not necessarily involve any alteration of the chemical state of nitrate ions. The concentrated waste streams or spent adsorbents generated from these removal methods are separately disposed. On the other hand, (bio)chemical reduction options aim to reduce nitrate ions to other states of nitrogen, e.g. ammonia, or a more innocuous form as nitrogen gas (Archna et al. 2012). Intermediate products such as nitrite, nitrous oxide and nitrogen dioxide may also be produced depending on the nature of treatment (Obiri-Nyarko et al. 2014).

**NATURAL ATTENUATION OF NITRATE IN SOIL AND GROUNDWATER**

Nitrate contamination of groundwater is governed by natural biogeochemical processes that control nitrate leaching into groundwater. Within the root zone of the topsoil, nitrogen fixation and nitrification processes make nitrogen available to plants in the form of ammonium (NH$_4^+$) and nitrate (Fang et al. 2007). Nitrate reduction may occur by plant uptake, mineralization-immobilization processes, volatilization, losses by run-off and denitrification (Shindo
& Nishio 2005; Chen et al. 2014). These processes, either as stand-alone or in combination, limits nitrate flux into groundwater. Notwithstanding, nitrate ions, unlike the positively charged NH$_4^+$ (that are bound to negatively charged soil particles), are loosely bound and may percolate beyond root zones into the phreatic zones of groundwater aquifer media (Salo & Turtola 2006; Rivett et al. 2008). Microbial denitrification is common in soils with over 60% pore saturation where oxygen for microbial respiration is limited (Abbasi & Adams 2000; Dobbie & Smith 2003). Microbial reduction of nitrate ion is a respiratory process that utilizes nitrate or nitrite as the terminal electron acceptor under conditions of limited oxygen supply. As a result adenosine tri-phosphate, a high energy molecule, is produced (Matejú et al. 1992; Hu et al. 2018). During this process, the electron transfer releases energy to the denitrifying bacteria for the synthesis of new cell biomass (Tong et al. 2013). Through the soil profiles, the complex biogeochemical processes have been reported to reduce the levels of nitrate reaching the groundwater. Figure 1 shows the processes of nitrogen transformation in the subsurface.

**BIOLOGICAL PROCESSES OF NITRATE REDUCTION IN GROUNDWATER**

**Heterotrophic denitrification of groundwater**

Nitrate removal from groundwater by biological processes has been widely studied and applied to remove nitrate from contaminated water. Autotrophic bacteria utilizes inorganic carbon sources and electron donors such as bicarbonates, carbon dioxide and sulphur compounds (S$^0$, H$_2$S, S$^{2-}$, S$_2$O$_3^{2-}$, S$_4$O$_6^{2-}$ and SO$_3^{2-}$) for cell synthesis (Qambrani et al. 2013). However, heterotrophic bacteria utilize complex carbon compounds as substrates for energy and cell synthesis (Rivett et al. 2008; Liu et al. 2013; Pous et al. 2018). In a natural heterotrophic reactive media, dissolved organic carbon, soluble and bioavailable carbon in pore waters of confined aquifer media may be used for denitrification. However, organic carbon insufficiency may limit the denitrification rate in such environments (Hiscock et al. 1991). Rivett et al. (2008) conceptualized that organic carbon sources, such as geologic organic matter (e.g.

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**Figure 1** | Nitrate cycling in the subsurface and pathway to groundwater.

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kerogen; a fossilized organic matter, plant residues, manures and organic contaminants, in the soil are degraded into simple bioavailable carbon compounds by different geochemical processes. The biodegradation of these organic components is achieved by different microbe-mediated processes. The resulting secondary products may contribute to the denitrification processes, serving as the carbon source. In addition, organic molecules exuded by the roots during translocation and fermentation of complex organic molecules (proteins, lipids and lignin) (Neff & Asner 2001) may also act as a carbon source for heterotrophic bacteria during denitrification processes in the sub-surface. From a practical viewpoint, slow release carbon sources are able to support extended denitrification applications in in-situ reactive media (Zhang et al. 2015).

Dissolved organic compounds naturally present in groundwater are only able to support small denitrification rates and thus, become the limiting agents in the denitrification process (Rivett et al. 2008). Therefore, small amounts of denitrification can only be achieved by the natural electron donors present in the subsurface groundwater. On the other hand, the addition of external carbon compounds also facilitates nitrate removal by denitrification. Low molecular weight compounds such as acetate were shown to be more reactive in denitrification processes compared to high-molecular weight compounds (Corre et al. 1999; Kaiser et al. 2002; Baker & Vervier 2004). Solid, liquid and gaseous state electron donors may also be used to achieve heterotrophic denitrification (Liu et al. 2013). Liquid state electron donors include: acetate, formate, sucrose, methanol, ethanol, starch, molasses (Hamazah & Ghararah 1996; Gómez et al. 2002; Ayyasamy et al. 2007) and vegetable oils (Hunter & Follett 1997). These types of organic carbon electron donors have been successfully and conveniently applied in many bio-denitrification studies. Such electron donors lead to advantageous and rapid denitrification. The use of methanol as an exogenous carbon source for denitrification follows the stoichiometric relationship shown in Equation (4):

\[ 6 \text{NO}_3^- + 5 \text{CH}_3\text{OH} \rightarrow \text{NO}_2^- + 5 \text{CO}_2 + 7 \text{H}_2\text{O} + 6 \text{OH}^- \] (4)

Notwithstanding, at the field scale, some of the disadvantages associated with liquid state exogenous organic carbon sources is the cost of continuous injection of the liquid organic carbon donor into the aquifer. Besides, other disadvantages include negative impact on geochemistry of aquifer, hazardous biomass build-up and clogging of fissures and pore spaces. Concerns about the formation of secondary carcinogenic amine compounds in acidic mediums may also prohibit the use of some liquid carbon electron donors (Samatya et al. 2006; King et al. 2012). Utilizing Acinetobacter bacteria (SYF26), Su et al. (2015) reported a 92% denitrification rate by using sodium acetate as electron donor. A C/N ratio of 4.31 was maintained at a pH of 7.3 and temperature of 29 °C. Denitrification in bio-sand filters (BSF) using ethanol as the external carbon source has been studied by Mutsvangwa & Matope (2017). The occurrence of denitrification in BSF takes place when biofilms develop on the surface of the sand media. In a recent study, Mutsvangwa & Matope (2017) reported an average nitrate removal efficiency of 44 and 53% for different C/N ratios of 1.1 and 1.8, respectively, at an influent nitrate concentration of 110.7 mg/L.

The gaseous organic carbon electron donor mainly used to catalyze denitrification is methane (Li et al. 2018). For in-situ nitrate remediation of groundwater, methane gas is pumped into the delineated plume to facilitate denitrification. Even though methane may be potentially inexpensive and is normally considered as a potential carbon source for biological denitrification, concerns of high pumping costs, unfavorable mass transfer rates, and the hazards in handling methane gas make it a less favored option for the majority of sub-surface denitrification operations (Liu et al. 2013). Jiang et al. (2018) used hydrogen as sole electron donor for denitrification and reduction of nitrate from groundwater co-contaminated with vanadium. About 91% denitrification was reported within 7 days and Dechloromonas and Hydrogenophaga species were reported as dominating microbial species involved in the removal process. Volatile fatty acids (VFA) produced from the oxidation of hydrogen served as carbon source for the denitrifying population to enhance denitrification.

Solid organic carbon donors used in the denitrification process include cellulose-based products and biodegradable polymers. The performance of crude cotton as a carbon source in biofilters for nitrate removal was studied by Aloni & Brenner (2017). In that study, nitrate removal was compared for two phases; a compressed cotton/beads medium (phase 1) and an uncompressed shredded cotton mixed with the beads.
(phase 2) in the biofilter column. The authors reported >95% nitrate reduction using a mixed sludge liquor from a water treatment plant, at a hydraulic loading rate of 0.1 L/min and biomass carrier density of 0.15 g/L for 60 days in the first phase. A second phase operation of the biofilter again reduced nitrate from 116.02 ± 13.85 to 38.53 ± 17.03 mg of nitrate. However, the production of a small amount of nitrite (0.17 ± 0.42 and 1.78 ± 0.87 mg/L in phases one and two, respectively) were reported at the bottom of the reactor. In the effluents of the first and second phases, respectively, 24.74 ± 6.43 and 2.32 ± 0.48 mg/L of TOC production was ascribed to the hydrolysis of cotton. However, in order to overcome nitrite accumulation and TOC production in the reactor, the authors recommended recirculation of the effluent. A carbon source with the capacity to sustain long term and stable denitrification rates is desirable for groundwater denitrification applications. Besides heterotrophic denitrification in the subsurface, many studies have also investigated the performance of solid, liquid and gas-phase carbon sources for heterotrophic denitrification of groundwater (Soares 2000; Li et al. 2018).

Table 1 shows a summary of the some of the previous studies of heterotrophic denitrification of groundwater. However, research focus is directed toward developing slow releasing polymers/carbon sources that are capable of sustaining denitrification rates over extended periods (Chu & Wang 2017). A slow releasing organic carbon source for denitrification was prepared from starch and polyvinyl alcohol (PVA). A denitrification efficiency of 88–97% was achieved using a packed bed bioreactor. The amount of COD consumed per nitrate nitrogen reduced (mg/mg) was reported to be 1.82–3.73 with average denitrification rates of about 0.2–0.4 g NO3/L·d at 20–29 °C.

Wu et al. (2012) developed a biodegradable polymer that serves as a carbon source and biofilm support for denitrification. Synthesized from 3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV) and polylactic acid (PLA), the PHBV polymeric slow-releasing carbon source was employed in a batch study to achieve a denitrification rate of 0.31 mg NO3/h. However, for a kinetic study in a continuous packed-bed reactor, 94.1% denitrification efficiency was reported for influent NO3 concentrations above 44.3 mg/L. An anoxic rotating biological contactor was used for biological denitrification of nitrate-contaminated oil refinery groundwater from Tehran, Iran by Mirbagheri et al. (2016). In their study, acetate was used as an external carbon source. The effect of hydraulic residence time (HRT), C/N ratio and nitrate loading rate on the nitrate removal was evaluated and the authors reported a nitrate removal efficiency of ~97%, at a nitrate concentration of ~100 mg/L, C/N ratio of 1.25 and HRT of 8 h.

**Autotrophic denitrification of groundwater**

Autotrophic denitrification of groundwater is widely considered to be cost effective, feasible to scale up and

<table>
<thead>
<tr>
<th>References</th>
<th>Temperature (°C)</th>
<th>pH</th>
<th>Influent concentration (mg NO3/L)</th>
<th>Hydraulic retention time</th>
<th>Electron donor</th>
<th>Nitrate removal (%)</th>
<th>Nitrate removal method</th>
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<tbody>
<tr>
<td>Liu et al. (2014)</td>
<td>15–33</td>
<td>7.3–8.3</td>
<td>103.9</td>
<td>16 d</td>
<td>Granulated spongy iron, zero-valent iron and pine bark</td>
<td>100</td>
<td>Autotrophic</td>
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<td>Su et al. (2016)</td>
<td>6</td>
<td>50</td>
<td>12 h</td>
<td>Iron (II)</td>
<td>9,500%</td>
<td>Autotrophic</td>
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<td>Pu et al. (2014)</td>
<td>6.7–6.5</td>
<td>56.69</td>
<td>6 d</td>
<td>Pyrite</td>
<td>&gt;99</td>
<td>Autotrophic</td>
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<td>Tourang et al. (2018)</td>
<td>25</td>
<td>7.4</td>
<td>150</td>
<td>Sodium thiosulfate</td>
<td>98–64</td>
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<td>Gómez et al. (2002)</td>
<td>15–20</td>
<td>7.0–7.5</td>
<td>50–70</td>
<td>31 d</td>
<td>Sucrose, ethanol and methanol</td>
<td>100</td>
<td>Heterotrophic</td>
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<td>–</td>
<td>417.1</td>
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<td>Ethanol</td>
<td>80</td>
<td>Heterotrophic</td>
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<td>Nurizzo &amp; Mezzanatte (1992)</td>
<td>400</td>
<td>Glucose syrup</td>
<td>80</td>
<td>Heterotrophic</td>
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<td>Hamazah &amp; Ghararah (1996)</td>
<td>240–1,300</td>
<td>Ethanol</td>
<td>95–97</td>
<td>Heterotrophic</td>
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selective, albeit a slow process when different nitrate removal options are considered (Gómez et al. 2002; Zhao et al. 2011; Tong et al. 2015). However, autotrophic denitrification produces less biomass and reduces the cost of post-treatment utilizing CO₂ and HCO₃⁻ as its carbon source for the synthesis of new cells. Bacteria from the genera Ferrobacillus, Gallionella, Leptothrix and Sphaerotilus were shown to carry out autotrophic denitrification using ferrous iron as the electron donor (Archna et al. 2012; Zhu & Getting 2012; Liu et al. 2013; Kiskira et al. 2017).

On the other hand, bacteria from the genera Paracoccus, Thiobacillus, Thiosphaera can use reduced sulphur compounds as the energy source for denitrification (Hiscock et al. 1991; Archna et al. 2012). Autotrophic denitrification occurs according to the following reactions (Equations (5) and (6)):

\[ 2 \text{NO}_3^- + 12 \text{H}^+ + 10 \text{e}^- \rightarrow \text{N}_2 + 6 \text{H}_2\text{O} \quad (5) \]

\[ \text{H}_2 + 0.35 \text{NO}_3^- + 0.35 \text{H}^+ + 0.052 \text{CO}_2 \rightarrow 0.010 \text{C}_5\text{H}_7\text{O}_2\text{N} + 0.17 \text{N}_2 + 1.1 \text{H}_2\text{O} \quad (6) \]

Denitrification rates can be significantly altered by pH (Rivett et al. 2008; Liu et al. 2013; Rout et al. 2017). Su et al. (2016) investigated the denitrification of groundwater by an autotrophic bacterial strain SY6 using Fe²⁺ and Mn²⁺ as electron donors in an immobilized biological filter reactor. Three influent nitrate concentrations of 10, 30, and 50 mg/L at pH = 6.0, 7.0 and 8.0 and HRT of 6, 8 and 12 h, respectively were used. An optimal nitrate removal of 95% was reported by the authors for Fe²⁺ at the influent nitrate concentration of 50 mg/L, HRT of 12 h and pH = 6.0. The stoichiometry of biological denitrification reaction in the presence of CO₂ (Equation (6)) suggests that denitrification rates may also be affected by the type of carbon source used. Table 1 shows a summary of some studies on nitrate removal from groundwater.

### Effect of process conditions on groundwater denitrification

#### Effect of dissolved oxygen

Bio-denitrification has been reported to occur under anaerobic conditions or under anoxic conditions (Eh values of −144 to +6.8 mV), at 140 m depth of groundwater (Katsuyama et al. 2013). Some denitrifiers such as Ochrobactrum sp. and Pseudomonas resinovorans have been reported to perform denitrification in oxygen depleted environments where nitrate ions are used as the electron acceptors (Lv et al. 2017). Bio-denitrification is favoured normally with dissolved oxygen (DO) concentrations below 0.5 mg O₂/L as is the case in many aquifers (less than 0.2 mg O₂/L in ideal cases) (Rivett et al. 2007). Gómez et al. (2002) asserted that even though small concentrations of DO can inhibit the bio-denitrification process, the effect of DO largely depends on the type of bacteria strain involved in the denitrification process. DO reduces denitrification enzyme activity. DO catalyses the reduction of nitrate and nitrous oxide reductase during denitrification (DeSimone & Howes 1998; Rivett et al. 2008). Consequently, molecular nitrogen production decreases and toxic intermediate products like nitrite are formed because of enzymatic inhibition.

#### Effect of temperature

Microbial growth rate in denitrification systems is influenced by various environmental conditions and physicochemical parameters such as the availability of substrate, pH, temperature, alkalinity, C/N ratio, presence of competing ions, and other natural chemicals. Among these, temperature has been a significant influence on the microbial denitrification rate. The high growth rate of denitrifying bacteria is related to temperature increase (Liu et al. 2013). Hoover et al. (2016) asserted that an increase in temperature will increase the reaction rates, specific rates and enzyme kinetics of a bacteria. In their study, the authors reported that denitrification rates increased with temperature between 5 and 30 °C for a woodchip (WC) bioreactor installed to reduce nitrate loads in agriculture drainage water. Moreover, their study noted that temperature coefficients of 2.6 to 2.9 were observed for denitrification rates of 9.72 to 12.82 mg NO₃/kg WC·d when temperature was increased from 10 to 20 °C at the influent nitrate concentration of 132 mg NO₃/L and HRT of 12.8 days. Similarly, Rivett et al. (2008) noted that denitrification typically occurs in a temperature range of 2 and 35 °C with optimal rates occurring between 25 and 30 °C. However, an increase in the reaction rate is also a function of the carbon source
available with highest growth rates obtained using methanol or acetic acid as carbon source. According to Gilbert et al. (2008) and Liu et al. (2013), the optimal temperatures for denitrification is between 25 and 35 °C. Foglar et al. (2004) illustrated the relation between temperature and denitrification using the Arrhenius equation (Equation (7)):

\[
k = A \times e^{(-E_a)/(R \cdot T)}
\]

where \( k \) = reaction rate, mg/L h, \( A \) = frequency factor, \( E_a \) = activation energy, kJ/mol, \( R \) = universal gas constant, kJ/mol K and \( T \) = temperature, K.

In Equation (7), the reaction rate constant varies exponentially with respect to the temperature. Typically, low temperatures will increase the acclimation period of denitrifying bacteria (Vacková et al. 2011). In the context of groundwater in the subsurface, typically, groundwater temperature varies with depth, geology and location. Shallow groundwaters are impacted by temperature from the surface which makes them warmer compared to water from deeper regions of the same aquifer. In northern parts of Europe, groundwater temperatures are usually in the range of ~10 to 15 °C. Hiscock et al. (1991) reported that denitrification rates drop at low temperatures, between 0 and 5 °C. Robertson et al. (2000) studied the performance of porous reactive barriers for the in-situ treatment of nitrate in groundwater over 6–7 years using cellulose solids as the carbon source at Killarney and Borden in Ontario, Canada. The authors reported 58–91% (~4.8 to 57 mg NO3/L) nitrate reduction over the period of the study. The study asserted that the nitrate consumption rates (~0.7 to 32 mg L NO3/d) in the porous reactive barriers were dependent on temperature. Hoover et al. (2016) investigated the effect of temperature on nitrate removal from agricultural drainage water using woodchip bioreactors (WC). The study reported that denitrification was lower at 10 °C than at 20 °C. The recommendations made by the authors from these studies show that low temperatures may slow down denitrification rates significantly.

Temperature coefficient, \( Q_{10} \) has also been used in the literature to study the relationship between nitrate removal rate and temperature (Hiscock et al. 1991; Davidson & Seitzinger 2006; Hoover et al. 2016). \( Q_{10} \) values, mainly used in the field, estimate the factor by which the denitrification rate increases for every 10 °C rise in temperature. Denitrification in river beds and sediments are influenced significantly by temperature. In streams and watersheds, nitrate reduction by denitrification process ranges from 10 to 70% (Appelboom et al. 2010).

**Effect of pH**

Biological denitrification processes are sensitive to pH fluctuations. Denitrification by heterotrophic bacteria mostly occurs in the pH range of 5.5–8.0 (Rivett 2008; Rout et al. 2017). Inhibition of denitrification may occur in highly acidic environments (Liu et al. 2013). Acidic conditions may result from the production of intermediary products from the oxidation of organic carbon sources. Heterotrophic denitrification is an alkaline producing process that alters the final reaction process to near neutral pH. Buffering mechanisms in carbonate aquifers may serve to control the acidification of the denitrification process.

**Effect of toxic inorganic compounds**

The presence of toxic inorganic compounds in groundwater have been shown to inhibit groundwater denitrification rates. Groundwater chemistry may be impacted through geogenic or anthropogenic influences that may result in significant concentrations of inorganic and organic toxic pollutants. The effects of heavy metals such as Cd(II), Cu(II), Ni(II), and Zn(II)) on aerobic denitrification rates carried out by the denitrifier strain *Pseudomonas stutzeri* PCN-1 was investigated by Guž et al. (2017). Heavy metal concentrations were shown to have an inhibition effect on aerobic denitrification activity and denitrifying gene expression. The authors ranked the influence of the heavy metals on aerobic denitrification according to the severity of inhibition as Cd(II) > Cu(II) > Ni(II) > Zn(II). Kiskira et al. (2018) also investigated the effect of Cu, Ni and Zn on Fe(II) mediated autotrophic denitrification. Prior to the introduction of the heavy metals, *Thiobacillus*-dominated mixed culture and *Pseudogulbenkiania* sp. 2002 were reported to achieve complete denitrification after 7 days. Alternatively, they used a pure culture of *T. denitrificans* which yielded 91–96% denitrification after 10 days of incubation. However, the addition of Cu, Ni and Zn at initial concentration of 5, 10, 20 and 40 mg/L resulted in reduction of denitrification to about 6, 8 and 6%,
respectively. The severity of inhibition induced by toxic inorganic pollutants in groundwater depends on the type and concentration of inorganic pollutants present in groundwater. Notably, the conditions of denitrification play a critical role in the inhibitory effects of heavy metal compounds on groundwater bio-denitrification since some heavy metals may concentrate and precipitate (e.g. hydroxide precipitation) when favorable pH is attained.

**Heterotrophic-autotrophic biofilm-electrode denitrification**

Zhao et al. (2011) investigated nitrate removal from groundwater by combining heterotrophic and autotrophic bacteria in a biofilm-electrode reactor. Treated water was reported to have low bacterial density. Similar studies by Tong et al. (2013) corroborated the effectiveness of using mixed autotrophic, heterotrophic bacteria and biofilm-electrode for denitrification of groundwater. The electrochemical effect of the system introduced a synergistic interaction between the hydrogenotrophic and heterotrophic bacteria to remove nitrate from groundwater. Dissolved CO₂ from the heterotrophic process was utilized as the inorganic carbon source by the autotrophic bacteria. Anodic carbon rods were embedded with stainless-steel wires, wherein the stainless-steel wires acted as cathodes to provide H₂ for hydrogenotrophic bacteria. Peng et al. (2018) evaluated the performance of a heterotrophic denitrification coupled with an electro-autotrophic denitrifying packed bed reactor (HEAD-PBR) in treating nitrate contaminated groundwater. The authors reported nitrate removal efficiency of about 99% for both 221.4 and 110.7 mg/L for an influent nitrate concentration in the HEAD-PBR reactor operated for 60 days at room temperature. The results of the study noted that groundwater nitrate removal using the HEAD-PBR technique was contributed to by electrolysis, heterotrophic denitrification, and autotrophic denitrification in the proportions of 15.6–23.4, 44.6–68.4 and 15.7–31.7%, respectively.

Microbial electro-remediation (MER) have been shown by many studies to achieve high nitrate removal from groundwater. Another advantage of the MER system is its application in groundwater contamination monitoring (Pous et al. 2018). Notwithstanding, Cecconet et al. (2018) asserted that cost components associated with MER may arise from energy consumption brought about by anolyte extraction and/or groundwater pumping (for ex-situ applications) for treatment.

**Membrane bioreactors**

Denitrification reactions can be carried out using membrane bioreactors. Conventional bio-denitrification methods have been reported as a cost effective, selective and feasible option for dealing with nitrate contaminated groundwater (Gómez et al. 2002). However, secondary treatment is often required in most cases to reduce the microbial load and the activated sludge present in the effluent (Gómez et al. 2002; Zhao et al. 2011). The effluents produced are usually turbid and with high organic carbon (secondary pollution) which are undesirable for drinking purposes. Further treatment is normally required in many cases (Sison et al. 1995; Buttiglieri et al. 2005; Zhao et al. 2011). Membrane-bioreactors are used to mitigate these conditions by allowing nitrate contaminated groundwater to pass through the lumen of a microporous membrane. Denitrification occurs on the shell side of the membrane as nitrate ions diffuse through the micropores. Fonseca (1999) studied the denitrification of nitrate polluted water at a concentration of 211.5 mg/L NO₃⁻ using a low flux filter (LFF), diafilter (DF) and ion exchange (IE) membrane bioreactors. Ethanol (1% w/v) was used as the carbon source. A surface denitrification rate and volumetric denitrification rate of 7.0 g NO₃⁻/d·m² and 65 g NO₃⁻/d·m³, respectively, was achieved by the IE membrane bioreactor. The LFF membrane bioreactors were operated continuously for 29 days. A nitrate removal rate of 100% was achieved at a volumetric denitrification rate of 240 g NO₃⁻/d·m³. The maximum nitrate removal by the DF membrane bio-reactor over 17 days of operation was 91% at a volumetric rate of 200 g·N·d⁻¹·m⁻³. Innovative membrane applications limit secondary pollution of treated water significantly.

**PHYSICO-CHEMICAL METHODS OF NITRATE REDUCTION FROM GROUNDWATER**

**Reductive denitrification by zero-valent iron**

Decomposition of nitrate ions can be achieved through chemical processes or a combination of biological and
chemical processes. Metals such as zero-valent iron (ZVI), elemental sulphur, zinc, chromium, cadmium, aluminium and lead can be used to chemically reduce nitrate in groundwater (Sabzali et al. 2006). Results from earlier studies suggested that pH and temperature are critical to attaining the right conditions for chemical reduction processes to occur. Chemical reduction of nitrate by nanoscale ZVI in an aqueous medium was studied by Yang & Lee (2005). Their study reported a complete reduction of nitrate in a 150 mg/L aqueous nitrate solution with a 2 g/L dose of ZVI in 45 min at pH = 3. In the same study, authors reported a nitrate reduction of 83% in 60 min for the same initial nitrate concentration and pH but for a lower adsorbent dose of 1 g/L. The results from their study suggested that nitrate reduction was an acid-driven surface-mediated process. The authors further posited that the nitrate reduction reaction involving ZVI under acid-controlled conditions (pH < 4) is a redox process. The study noted that chemical nitrate reduction was achieved by the free electrons donated from the surface of nano-sized ZVI through the corrosion of metallic iron at strong acidic pH. Nitrate was reduced by the ZVI according to Equations (8)–(10). The successful application of ZVI as a denitrifica-
tion agent was due to its electron donating property (Shrimali & Singh 2001). Sabzali et al. (2006) studied chemical denitrification using batch experiments coupled with catalytic cells. Zn metal was used as a catalyst and sulfamic acid (H2NSO3H) was added stoichiometrically as spent reagent. A nitrate concentration of 130 mg/L in natural groundwater samples from Firouzkooh, Tehran and synthetic groundwater was used. More than 99% nitrate reduction was reported. However, there was an increase in the sulphate and chloride ion concentrations due to the sulphamic ion and electrolysis process that reduced Zn2+ to Zn0. The catalytic reduction and chemical denitrification reactor (ChemDen reactor) was earlier proposed by Dzie-
winski & Barber (1999). Though high nitrate reduction achieved was desirable, post-treatment of effluent is usually still required for drinking use:

\[
3 \text{NO}_3^- + 8 \text{Fe(OH)}_2 + 6 \text{H}_2\text{O} \rightarrow 3 \text{NH}_3 + 8 \text{Fe(OH)}_3 + \text{OH}^- \quad (8)
\]

\[
\text{NO}_3^- + 4 \text{Fe}^0 + 10 \text{H}^+ \rightarrow 4 \text{Fe}^{2+} + 3 \text{NH}_4^+ + 3 \text{H}_2\text{O} \quad (9)
\]

\[
2 \text{NO}_3^- + 5 \text{Fe}^0 + 12 \text{H}^+ \rightarrow 5 \text{Fe}^{2+} + N_2(g) + 6 \text{H}_2\text{O} \quad (10)
\]

Suzuki et al. (2012) investigated the mechanisms of nitrate reduction by ZVI using batch experiments. The effects of pH (2.5 and 4.5), solid–liquid ratio, initial concentration of nitrate augmented ferrous ion (50 mg NO3/L and 200 mg Fe/L) and contact time (1, 3 and 6 h) on nitrate reduction efficiency by ZVI were evaluated. It was observed that electron transfer from ZVI was favoured via magnetite (corrosion product) layer production during ZVI reaction with the aqueous medium. The study further concluded that ZVI coated with magnetite reduces nitrate to ammonium (near neutral pH) when the oxidized iron (Fe2+) is adequately augmented in the aqueous phase. Aluminium powder has also been applied to remove nitrate from groundwater by Murphy (1991). In that study, aluminium powder was used to reduce nitrate to ammonia, nitrogen and nitrite. Nitrate was selectively reduced in the pH range of 9.0–10.5. No reduction, however, was observed at a pH value of 8.0 because of the formation of aluminium oxide coating on the aluminium particles.

Xu et al. (2017) investigated the nitrate reduction performance of aluminium-iron alloys in aqueous solution within a wide pH range (2.0–12.0). About 40% nitrate selectivity at neutral pH was reported for aluminium-iron alloy with 58% iron composition and 60% nitrate selectivity for 20% iron containing alloy. Bao et al. (2017) reported 20% nitrate selectivity for warm water (45 °C) activated aluminium-iron alloy. The aluminium-iron alloy (5 g/L) was applied to aqueous solution having an initial nitrate concentration of 50 mg/L, in the pH range of 5.0–6.0, and 97.6% nitrate was reduced to NH4 by microscale ZVI (Lee et al. 2017).

A nanoscale ZVI (nZVI) has been reported to be attractive for denitrification due to their higher specific surface area and higher surface reactivity. Peng et al. (2015) used a mathematical model to evaluate the performance of an nZVI in microbial denitrification of groundwater. The study integrated chemical abiotic nitrate reduction with nZVI (i.e. nZVI corrosion for hydrogen production and hydrogen-based microbial reduction of denitrification). Microbial nitrate reduction and interactions in the system, ammonium accumulation and hydrogen turnover were described by the model. The authors suggested an nZVI dosing of 3–6 mmol/L in temperature range of 30–40 °C,
6–10 mmol/L in the temperature range of 15–30 °C and 10–14 mmol/L in the temperature range of 5–15 °C during groundwater remediation to ensure a low ammonium yield and a high nitrogen removal efficiency.

**Ion exchange processes**

Ion exchange processes have been utilized in groundwater remediation in many parts of the world. Strong base anion exchange resins provide sites for the exchange of chloride and bicarbonate ions with nitrate from the aqueous contaminated water (Matošić et al. 2000; Núñez et al. 2017). The application of ion exchange technologies using strong base exchange resins of triethylamine functional groups showed a selective ion exchange affinity in the order bicarbonate < chloride < nitrate < phosphate. These resins were specially designed with a high number of carbon atoms around ammonium nitrogen functional groups to increase the nitrate selectivity (Matošić et al. 2000; Samatya et al. 2006). The ability to regenerate the spent resins for reuse makes it economically attractive for water treatment (Archna et al. 2012).

**Reverse osmosis**

Reverse osmosis (RO) technology is used in pump and treat (P&T) applications to remove nitrate from groundwater. In the RO process, contaminated groundwater is extracted and pumped through reverse osmosis cells under high pressure (ca 300–1,500 psi) (Archna et al. 2012). Similar to ion exchange technology, reverse osmosis may be used for saline nitrate impacted groundwater. As an example, reverse osmosis technology has been widely applied for nitrate removal from drinking water in South Africa (Schoeman & Steyn 2003). However, the operational costs, membrane fouling and deterioration, as well as maintenance of the RO system, may pose challenges which must be considered. Furthermore, issues concerning the disposal of brine effluent from the RO process should also be addressed.

**Adsorption-based processes**

Groundwater treatment technologies adopt ion-exchange processes, reverse osmosis, adsorption, electro-dialysis, chemical methods and biological methods for the treatment of nitrate. Most of the nitrate removal techniques were found to be cost-intensive and produce other by-products or chemicals which require secondary treatment of the effluent. The adsorption process has been studied extensively in the literature. Compared to the other processes, the adsorption process has been shown to be efficient, requires less cost, less energy requirements and has a wider application in nitrate removal from groundwater (Bhatnagar et al. 2008). Adsorbents evaluated in the literature include carbon-based sorbents such as powdered and granular activated carbon (Bhattacharyya & Gupta 2008; Khani & Mirzaei 2008). Clay, zeolites and sepiolites have also been used to remove nitrate from water. Other adsorbents reported in the literature include sorbents made from organic matter residue and industrial wastes such as fly ash, red mud, slag, bamboo powder, chitosan, mesoporous silica, cement paste, and nano-alumina can be used for nitrate removal from groundwater. Mehrabi et al. (2015) studied the nitrate removal efficiency of two adsorbents: activated carbon and composite Fe2O3 activated carbon nanoparticles from water. The authors used response surface methodology and central composite design to predict optimal parameter conditions for nitrate removal. For the activated carbon, 68.45% nitrate removal efficiency was reported for an adsorbent dose of 0.53 g/50 mL, initial concentration of 147.31 mg/L and pH of 3.0. A nitrate removal efficiency of 95.5% was also reported for the adsorbent dose of 0.53 g/50 mL, pH of 5.1 and initial concentration of 69.16 mg/L. The authors noted that the adsorption of nitrate ion by both the activated carbon and the Fe2O3 activated composite adsorbent followed the Langmuir monolayer adsorption isotherm with the latter having a higher sorption capacity. A polystyrene resin (NDQ), modified with amino and quaternary ammonium groups, was used by Wang et al. (2015) to adsorb nitrate from water. The results from the batch study reported by the authors showed that the modified NDQ exhibited a monolayer adsorption isotherm with maximum adsorption capacity for nitrate as 211.8 mg/g at initial nitrate concentration of 1,000 mg/L, adsorbent dose of 0.1 g/50 mL and contact time of 24 h.

The desirability of an adsorbent for nitrate adsorption depends on the high surface area and active sites available.
for the adsorption of nitrate ions. In some cases, surface modification of sorbents is required to increase their adsorption capacity. Bhatnagar & Sillanpää (2011) reviewed various adsorption media for nitrate removal in water. A general classification of adsorbents used for nitrate removal from water is presented in Table 2. There is continuous effort made by researchers to develop low cost adsorbents with high sorption capacity. Various adsorbents studied in the literature have varying capacities to adsorb nitrate from drinking water. However, these experiments were not carried out under field conditions. Nitrate removal under field conditions where multi-component pollutants are available influences the efficacy of the adsorbents. Limited study has been done to understand the influence of co-pollutants in groundwater on the removal efficacy of adsorbents for nitrate removal from groundwater.

The literature is proliferated with studies on the use of various adsorbents for nitrate removal from water. Adsorbents studied include zeolite, clay, sepiolite, activated carbon, chitosan, etc. (Öztürk & Bekta 2004; Namaisamyam & Sangeetha 2005; Arora et al. 2010; Xi et al. 2010; Li et al. 2017; Elmelouky et al. 2018; He et al. 2018; Satayeva et al. 2018). The use of coconut shell to prepare granular activated carbon for adsorption of nitrate in water has been studied extensively in the literature. Bhatnagar et al. (2008) studied the nitrate adsorption characteristics of treated and untreated granulated activated carbon from coconut. Groundwater nitrate concentration in the range of 5–200 mg/L at 25°C and pH of 5.5 was used for batch studies. The study concluded that ZnCl2 treated coconut husk shows a higher nitrate adsorption capacity of 10.2 mg/g compared to 1.7 mg/g adsorbed by untreated coconut husk. In another study, Das et al. (2015) delineated how to prepare activated carbon from coconut shell to achieve good adsorption properties. In that study, the authors also examined the physical and chemical properties of activated carbon produced from green coconut shell. It was concluded that activated carbon from coconut shell shows a microporous structure with improved surface area of 921 m²/g.

Activated carbon is produced mainly from carbonaceous materials. The choice of a suitable precursor used is dependent upon the purity of activated carbon desired and the yield. The presence of surface functional groups, the temperature and pH during the adsorption process also contribute to the adsorptive performance of activated carbon. With extensive pore size distribution and large surface area ranging from 500 to 2,000 m²/g, activated carbon provides active sites for attachment of molecules (Mohd Din et al. 2009). However, the adsorptive capacity depends on the precursor used and the adsorbent preparation method (material and activation method used) (Peláez-Cid & Teutli-León 2012). A summary of various adsorbents used for nitrate adsorption, process parameters and nitrate removal efficiencies is shown in Table 2.

Table 2 | Summary table of various adsorbents used for the adsorption of nitrate, their process parameters and performance

<table>
<thead>
<tr>
<th>pH</th>
<th>Temperature (°C)</th>
<th>Contact time</th>
<th>Influent concentration (mg NO₃⁻/L)</th>
<th>Amount adsorbed (mg/g)</th>
<th>Adsorbent</th>
<th>Nitrate removal method</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5</td>
<td>25</td>
<td>2 h</td>
<td>5–200</td>
<td>10.2</td>
<td>ZnCl₂ coconut husk GAC</td>
<td>Adsorption</td>
<td>Bhatnagar et al. (2008)</td>
</tr>
<tr>
<td>5.5</td>
<td>25</td>
<td>2 h</td>
<td>5–200</td>
<td>1.2</td>
<td>Untreated coconut GAC</td>
<td>Adsorption</td>
<td>Bhatnagar et al. (2008)</td>
</tr>
<tr>
<td>30</td>
<td>48 h</td>
<td>1–30</td>
<td>87.42</td>
<td></td>
<td>Sugarcane bagasse</td>
<td>Adsorption</td>
<td>Orlando et al. (2002)</td>
</tr>
<tr>
<td>&lt;8</td>
<td>5</td>
<td>1 h</td>
<td>100–700</td>
<td>46.6</td>
<td>Ammonium functionalized meso-structured silica</td>
<td>Adsorption</td>
<td>Hamoudi et al. (2007)</td>
</tr>
<tr>
<td>10</td>
<td>120 h</td>
<td>0–10</td>
<td>1.25</td>
<td></td>
<td>Bamboo charcoal powder</td>
<td>Adsorption</td>
<td>Mizuta et al. (2004)</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>24 h</td>
<td>25–1000</td>
<td>90.7</td>
<td>Chitosan beads</td>
<td>Adsorption</td>
<td>Chatterjee et al. (2009)</td>
</tr>
<tr>
<td>30</td>
<td>48 h</td>
<td>1–30</td>
<td>80.6</td>
<td></td>
<td>Rice hull</td>
<td>Adsorption</td>
<td>Orlando et al. (2002)</td>
</tr>
<tr>
<td>15</td>
<td>10 min</td>
<td>0–25</td>
<td>1.22</td>
<td></td>
<td>Commercial activated carbon</td>
<td>Adsorption</td>
<td>Mishra &amp; Patel (2009)</td>
</tr>
<tr>
<td>5</td>
<td>5 min</td>
<td>100</td>
<td>38.16</td>
<td></td>
<td>Sepiolite activated by HCl</td>
<td>Adsorption</td>
<td>Öztürk &amp; Bekta (2004)</td>
</tr>
<tr>
<td>&lt;5</td>
<td>25</td>
<td>1 h</td>
<td>620</td>
<td></td>
<td>Powdered activated carbon</td>
<td>Adsorption</td>
<td>Khani &amp; Mirzaei (2008)</td>
</tr>
</tbody>
</table>
APPLICATION OF DIFFERENT NITRATE REMOVAL TECHNOLOGIES FOR GROUNDWATER REMEDIATION

Ex-situ nitrate removal from groundwater by the pump and treat method

Groundwater exploitation and groundwater contamination is experienced globally. A wide range of in-situ and ex-situ technologies have been proposed by researchers for the removal of nitrate from groundwater. The ex-situ treatment option primarily involves the P&T method consisting of extraction of contaminated groundwater, treatment and discharging the water back into the aquifer via reinjection or percolation. This method has been used in superfund sites in the United States for remediation of organic polluted aquifers. This application is most effective when contaminant plume can be well defined (US EPA 2005; Faris 2009; King et al. 2012). The P&T method can also be applied to treat groundwater heavily contaminated with nitrate, however, the cost involved is a disincentive.

King et al. (2012) reported that the treatment of nitrate in groundwater by the P&T method may not be achieved within a single cycle of operation. In such cases, the P&T method may require more than one cycle to treat nitrate containing groundwater since re-mixing of the treated water from high conductive zones of the aquifer may mix with the untreated water from low conductive zones, resulting in recontamination. In addition, limitations of site characteristics, co-contaminants availability, operation and maintenance, scale of operation and many more options are disadvantages to the application of this technology for sustainable water treatment. Practically, the ex-situ P&T method is considered capital intensive and hardly applicable in low funding projects. Upscaling of such technologies requires huge funding options. As a result, it is regarded unsustainable.

Studies by Blowes et al. (1994), Robertson & Cherry (1995), Moorman et al. (2010) and Schipper et al. (2010), have reported the P&T approach for reducing nitrate concentrations in groundwater. However, these studies used above-ground wood chip bioreactors (WCBRs) for the treatment of nitrate. WCBRs induce biochemical oxygen demand (BOD) in the influent groundwater, therefore depleting oxygen from the water to allow denitrifying bacteria to flourish and perform nitrate treatment in WCBRs. Although this approach was reported to be efficient in reducing nitrate concentrations, WCBR are only applicable in practice to shallow depths of \( \sim 1-3 \) m. The cost and supply of wood chips and the electrical cost involved in pumping are also disincentives to the adoption of this technology (King et al. 2012). The effluent after treatment requires post-treatment to meet the drinking water standards due to impartation of unintended contaminants (Blowes et al. 1994; Moorman et al. 2010; Schipper et al. 2010). Leverenz et al. (2010) studied variations of WCBR using cattail, Typha sp. Phytoremediation options have also been explored in the literature by using plant species capable of nitrate uptake from pumped groundwater used for irrigation and reinjection back to groundwater. This approach has been found to be suitable for wetlands and shallow phreatic zone groundwater's compared to deep groundwater systems (Horne 2000).

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

In-situ bioremediation is used in passive nitrate treatment of polluted groundwater. In-situ technologies can limit the cost of pumping out, treatment and reinjection. In-situ technologies are achieved by intercepting the contaminant plumes with treatment systems that undertakes denitrification in the sub-surface. Remediation options using enhanced in-situ biological denitrification (EISBD) and permeable reactive barriers (PRBs) use carbon substrates which serve as electron donors in the denitrification step. Despite the relative advantages of these methods over ex-situ methods, their effectiveness and comparative advantages hinge on the utilization of cost effective carbon substrate (ITRC 2002).

Intercepting the appropriate flow path of the contaminant plume, degree of accuracy of predicting sub-surface heterogeneous characteristics and flow parameters, and availability of sufficient reactive site in contact with the contaminant plume are challenges for the application of this technology in practice (King et al. 2012). Notwithstanding, research has shown that PRBs are effective technology in removing contaminants in groundwater. In-situ, passive remediation technology has been used to successfully
remove heavy metals and other hazardous compounds from groundwater in superfund sites (ITRC 2002). The basic schematic concept of installation and operation of a PRB is shown in Figure 2.

PRBs have been suggested by researchers as a good nitrate remediation technology for contaminated groundwater (Robertson & Cherry 1995; Robertson & Vitousek 2009). Schipper et al. (2010) demonstrated that denitrifying bioreactors can be used to remove nitrate, pathogens and pharmaceutical compounds from groundwater. In their study, solid carbon substrates were used to decontaminate nitrate polluted groundwater. However, in similar studies, concerns of pollution swapping and long-term effectiveness of PRBs have been reported as deficiencies of PRB technology (Rivett et al. 2008; Heaton et al. 2012). Subsequent researches have revealed that pollution swapping problems could be removed or dealt with by use of multi-barrier systems using permeable reactive interceptors. In long-term field trials (>10 years), Robertson & Vitousek (2009) also showed that PRBs constructed using a mixture of sand and sawdust can remove 50–100% of nitrate from groundwater.

The literature asserted that the adoption of autotrophic, heterotrophic or mixotrophic systems do achieve good nitrate removal levels. Moreover, selection of suitable materials for PRB as electron donors with long-term reactive life is necessary for denitrification and performance of the system. Appropriate electron donating media of PRB facilitates nitrate removal through chemical oxidation, ion exchange processes or adsorption processes (in mixed media PRBs) in groundwater as it passes through the media of the PRB. The efficiency of nitrate removal is influenced by the particle size, surface area and surface chemistry. The literature has shown that HRT, pH and the type of media for PRB significantly influence the performance of PRB. In summary, nitrate removal from groundwater can be achieved by using different methods. Various studies have reported about the adsorption behaviour of several adsorbents and their capacities to remove nitrate from groundwater (Table 2). The various adsorbents presented in the literature show varying sorption capacities to remove nitrate under varying process conditions of temperature, pH, influent initial concentration, type of electron donor (in the case of biological denitrification) and HRT. Considering adsorption processes, process parameters such as pH, initial concentration of nitrate in solution, contact time and adsorbent time were shown to influence adsorption capacity.

For in-situ groundwater denitrification, the carbon electron donors must be able to support denitrification for

![Figure 2](https://iwaponline.com/aqua/article-pdf/67/8/885/519111/jws0670885.pdf)

**Figure 2** | Permeable reactive barrier for groundwater nitrate remediation.
longer durations without any limiting conditions (Oa et al. 2006). Organic carbon source electron donors used for denitrification purposes must have average reactivity, must be able to support extended periods of denitrification, be affordable, easily accessible and easy to handle. Smith et al. (2001) simulated groundwater denitrification under in-situ conditions using sodium formate as electron donor. The sodium formate was added to sand and gravel aquifers of Cape Cod, Massachusetts and denitrification rates were monitored. Groundwater was abstracted and amended with formate and bromide and subsequently injected back into the aquifer. Using multilevel samplers up to 15 m of transport by natural gradient flow, the authors noted that 80–100 and 60–70% reductions were observed for nitrate and formate, respectively. Further, a two-dimensional site specific model was used to model transport, denitrification and microbial growth on a laboratory scale. Aquifer media was used to predict the breakthrough curves. The results showed that formate enhanced by nitrite consumption was about four times slower than nitrate reduction but was completely consumed in the laboratory scale.

**CONCLUSIONS**

The global impact of nitrate contamination in most of the groundwater aquifers is a topic of major health and environmental concern. Innovation in water treatment technologies that are environmentally friendly, economical and easily scalable remains the future of water treatment technologies. Nitrate movement into groundwater is significantly influenced by the influent recharge conditions as well as the prevailing biogeochemical processes. The natural pathways of nitrate attenuation in the subsurface evidenced in the literature showed small reductions in nitrate concentration in groundwater compared to active and passive methods employed in treating nitrate contaminated groundwater. On the other hand, nitrate treatment methods reported in the literature show varying nitrate removal efficiencies from the groundwater. In the case of ex-situ groundwater nitrate removal technologies, concerns about secondary pollution is one of the major challenges that still needs to be addressed. A thorough understanding of groundwater flow regimes and contaminant transport properties are crucial for the successful application of PRBs for nitrate remediation. Aquifer heterogeneity plays a pivotal role in accurate delineation of contaminant plume for subsequent remediation applications.

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