



Review Nitrate Removal by Zero-Valent Metals: A Comprehensive Review

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Abstract: Nitrate is a widespread water contaminant that can pose environmental and health risks. Various conventional techniques can be applied for the removal of nitrate from water and wastewater, such as biological denitrification, ion exchange, nanofiltration, and reverse osmosis. Compared to traditional methods, the chemical denitrification through zero-valent metals offers various advantages, such as lower costs, simplicity of management, and high efficiencies. The most utilized material for chemical denitrification is zero-valent iron (ZVI). Aluminium (ZVA), magnesium (ZVM), copper (ZVC), and zinc (ZVZ) are alternative zero-valent metals that are studied for the removal of nitrate from water as well as from aqueous solutions. To the best of our knowledge, a comprehensive work on the use of the various zero-valent materials that are employed for the removal of nitrate is still missing. Therefore, in the present review, the most recent papers concerning the use of zero-valent materials for chemical denitrification were analysed. The studies that dealt with zero-valent iron were discussed by considering microscopic (mZVI) and nanoscopic (nZVI) forms. For each Fe⁰ form, the effects of the initial pH, the presence or absence of dissolved oxygen, the initial nitrate concentration, the temperature, and the dissolved ions on the nitrate removal process were separately evaluated. Finally, the different materials that were employed as support for the nanoparticles were examined. For the other zero-valent metals tested, a detailed description of the works present in the literature was carried out. A comparison of the various features that are related to each considered material was also made.

Keywords: chemical denitrification; nitrate; zero-valent aluminium; zero-valent copper; zero-valent iron; zero-valent magnesium; zero-valent zinc

1. Introduction

Nitrogen compounds are released into the environment from several anthropogenic sources, which causes an imbalance between the availability of nitrogen and the need for this element in ecosystems. In particular, ammonium (NH_4^+) , nitrite (NO_2^-) , and nitrate (NO_3^-) are the most common forms of reactive nitrogen in aquatic ecosystems [1]. The anthropogenic sources of nitrogen compounds can be divided into point and nonpoint sources [1]. Point sources are represented by the wastewater from livestock farms, industrial and municipal wastewater effluents, runoff, infiltrations from waste disposal sites, and more [1]. Nonpoint sources, which generally are more dangerous and problematic to control because of their extension, include cultivations of N₂-fixing crop species, runoff from agricultural lands fertilized with animal manures and synthetic fertilizers, runoff from burned or N-saturated forests, emissions from the combustion of fossil fuels, etc. [1].

Although nitrogen is an essential element for plants and other living beings, an excessive presence of nitrogen compounds in the environment is responsible for pollution phenomena. In particular, nitrate is associated with the eutrophication of water bodies, which is an excessive enrichment of nutrients (phosphorus and nitrogen). This causes a disproportionate growth of algae and other aquatic plant species, which, when they die,



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). are decomposed by microorganisms, which causes a lack of dissolved oxygen in the water. The negative effects of this phenomenon include the lowering of the aesthetic value of the lakes, undesirable odours, and the destruction of aquatic life [2].

Furthermore, drinking nitrate-contaminated water is linked to certain health issues. Indeed, nitrate can cause methemoglobinemia in infants, which is also known as "blue baby syndrome". Methaemoglobin is formed when the ferrous ion in haemoglobin is oxidized to the ferric form by nitrite, which is produced from the endogenous bacterial conversion of nitrate [3]. Methaemoglobin is unable to bind oxygen and, for this reason, methemoglobinemia manifestations include cyanosis, stupor, and cerebral anoxia [3]. Moreover, nitrate is associated with the formation of N-nitrosamines, which are considered carcinogenic compounds. For this reason, the International Agency for Research on Cancer (IARC) has classified ingested nitrate or nitrite as probably carcinogenic to humans (Group 2A) [4].

Several techniques have been developed for the removal of nitrate from water, as well as from wastewater and waste streams. Traditionally, nitrate is removed from water by exploiting biological denitrification [5], ion exchange [6,7], nanofiltration (NF) [8,9], and reverse osmosis [10,11].

Although biological denitrification is largely applied for the denitrification of wastewaters and is relatively cheap, the possible presence of residual organic matter and bacterial contamination are important limitations to the application on drinking water.

The ion exchange processes produce a waste brine that needs post treatments, with additional costs [7]. Further complications linked to this technique are "nitrate dumping" and the lower affinity for nitrate, as compared to sulphate, in some resins [6].

One of the most problematic features for NF, as for any membrane separation process, is represented by the fouling phenomenon. In the NF process, this problem may be more complex because of the kind of interactions that take place at the nanoscale [9]. Furthermore, nitrate is partially removed by nanofiltration since it is a monovalent anion [9].

Reverse osmosis allows for the concentration of the contaminant in a waste brine without modifying its molecular structure, and it is suitable for drinking water [11]. However, this concentrated brine may pose a disposal problem [11]. Moreover, the reverse osmosis membranes are subjected to fouling, compaction, and deterioration problems [10].

The chemical denitrification of nitrates through zero-valent metals has aroused great interest, due to its several advantages, such as the simplicity of management, the relatively low costs, the high efficiency, and the possibility of transforming pollutants into less dangerous forms. Therefore, several materials have been tested over time.

Zero-valent iron (ZVI) is the most investigated among the zero-valent metals, since it is cheap, easily available, and abundant [12]. Indeed, ZVI has been applied for the removal of a wide variety of contaminants, such as heavy metals [13], dyes [14], chlorinated organic compounds [15], and nitrate [16].

In particular, zero-valent iron has been demonstrated to successfully reduce NO_3^- [16]. Commonly, to enhance iron reactivity, the reduction of nitrate is carried out under acidic conditions of pH [17,18]. However, the addition of acids may lead to higher operational costs and to a greater content of anions in the effluent, which can pose a health risk [18].

The use of zero-valent iron nanoparticles (nZVI) has been shown to enhance process performances. Indeed, nanoparticles, thanks to their small size, are characterised by a large surface area and, thus, by a higher reactivity than microscopic iron (mZVI) [17,19,20]. Furthermore, several studies have experimented with the possibility of supporting nanoparticles on various matrices, such as inorganic clay minerals [21], activated carbons [22], graphene [23], and biochar [24].

In addition to Fe⁰, other zero-valent metals have been tested over time. Among these metals, zero-valent aluminium (Al⁰) is the most studied [25–29]. However, there are some drawbacks, which include the need for a high pH and the presence of Al³⁺ ions in the treated water [26]. Some studies have reported the reduction of nitrate by means of zero-valent magnesium (Mg⁰), whose reaction product (Mg²⁺) does not pose health risks [17,30–34]. Furthermore, more recently, other zero-valent metals, such as copper (Cu⁰)

and zinc (Zn^0), have been tested for nitrate removal [35–40]. These works testify to the interest of the scientific community in the development of alternative zero-valent metals that are suitable for nitrate abatement.

Despite this, in the literature, it is possible to find papers that are mainly focused on the review of nitrate removal by ZVI. On the other hand, there is a lack of papers that critically analyse the advances in the application of other metals for chemical denitrification. In particular, to the best of our knowledge, there is no review that comprehensively examines the use of various zero-valent metals. Therefore, the aim of this study is to provide a complete framework on the metallic elements that have been tested for nitrate removal in order to help readers in the evaluation of the applicability of the different materials, and to plan further research on this topic. In this regard, in addition to the chemical denitrification through zero-valent iron, the reduction processes with aluminium, magnesium, copper, and zinc are examined. The effect of the main operating parameters are analysed and discussed. Finally, a comparison between the advantages and drawbacks of the materials is made.

2. Removal of Nitrate by Means of Zero-Valent Iron

Several studies report the effective removal of nitrate by zero-valent iron particles [41–44]. The most investigated ZVI forms in chemical denitrification are mZVI and nZVI. Both microscopic and nanoscopic iron efficiencies are influenced by the operating conditions. Therefore, the following subsections are divided according to the dimensions of the iron particles (microscopic or nanoscopic) and the impact on the process of the main operating parameters.

2.1. Microscopic Iron

The process of nitrate removal by means of mZVI is affected by several parameters, the most important of which are the pH, the temperature, the dissolved oxygen, the initial nitrate concentration, and the dissolved ions. In the present section, the effects of these parameters are discussed.

2.1.1. Effect of pH

The importance of pH on the chemical denitrification through Fe⁰ is shown by several authors. Huang et al. analysed the process considering both uncontrolled and controlled pH conditions [16]. The tests without pH control were conducted for the initial pH values ranging between 2 and 11, with no further corrections. Although 95% of the nitrate was removed in less than 30 min at an initial pH of 2, no reduction occurred for pHs > 4 within 10 h. Moreover, the tests showed a rapid increase in the solution pH, which, in the first 30 min of treatment, increased by about two units, and then reached an asymptotic value. Such trends suggest that the reduction in the nitrate occurred within the first minutes of treatment, while a simultaneous oxidation of Fe^0 led to the inactivation of the material. Consequently, it can be assumed that low pH values are favourable for the process. This was also confirmed by the results of the experiments that were conducted by holding the pH at acid values (2.5, 3, 4, and 4.5) during the entire treatment, in which a significant enhancement in the nitrate removal was achieved [16]. Therefore, the authors supposed that protons directly participate in the chemical reduction of NO_3^- , or that they indirectly promote it [16]. This hypothesis has been confirmed by numerous works in which the mechanisms of chemical denitrification are proposed. Different reactions occur during nitrate removal through Fe^0 (Equations (1)–(5)). In particular, the reduction of NO_3^- can lead to the production of ammonium [45,46]:

$$4Fe^{0} + NO_{3}^{-} + 10H^{+} \rightarrow 4Fe^{2+} + NH_{4}^{+} + 3H_{2}O$$
⁽¹⁾

or nitrite [46]:

$$Fe^0 + NO_3^- + 2H^+ \rightarrow Fe^{2+} + NO_2^- + H_2O$$
 (2)

Moreover, ammonium can be generated by the reduction of nitrite [46]:

$$3Fe^{0} + NO_{2}^{-} + 8H^{+} \rightarrow 3Fe^{2+} + NH_{4}^{+} + 2H_{2}O$$
 (3)

and by the reduction of NO_3^- , which is operated by the H₂ produced by iron corrosion [47]:

$$2\mathrm{H}^{+} + \mathrm{Fe}^{0} \rightarrow \mathrm{H}_{2} + \mathrm{Fe}^{2+} \tag{4}$$

$$NO_3^- + 4H_2 + 2H^+ \to NH_4^+ + 3H_2O$$
 (5)

From Equations (1)–(5), it emerges that acidic conditions enhance the reduction of nitrate. Indeed, protons are needed to promote the oxidation of iron and to favor the deoxidization process of NO_3^- [48].

Furthermore, during the reduction of nitrate through Fe^0 , the production of nitrogen gas (N₂) can occur with the formation of OH⁻, the accumulation of which can be avoided with the H⁺ supply [46,48]:

$$5Fe^0 + 2NO_3^- + 6H_2O \rightarrow 5Fe^{2+} + N_2 + 12OH^-$$
 (6)

$$10Fe^{0} + 6NO_{3}^{-} + 3H_{2}O \rightarrow 5Fe_{2}O_{3} + 3N_{2} + 6OH^{-}$$
(7)

Hao and Zang, when using Fe⁰ in combination with a catalyst (diatomite coated with Pd and Sn), reported both ammonium and nitrogen gas as reaction products [48]. In particular, although the abatement of NO_3^- was 96% at a pH of 2.1, most of the nitrate that was removed was converted to NH_4^+ [48]. On the other hand, the N₂ selectivity was gradually increased until a pH of about 5 was reached, and was then drastically decreased, reaching 26% at a pH of 7.3. Therefore, the production of ammonium or nitrogen gas also depends on the pH of the solution (see Equations (1)–(7)). Indeed, under strong acidic conditions, the generation of ammonium mainly occurred, while a pH of around 5 improved the N₂ production and inhibited the ammonium formation [48].

Despite these aspects, many other authors found strongly acidic pH conditions to be optimal for nitrate denitrification [47]. Indeed, Hao et al. (2005), using scrap iron filings, observed an efficiency near to 80% after 240 min of treatment, when the initial pH was adjusted to 2.5. For a pH of 4, the abatement was lower than 10% [47].

Other authors have also performed chemical denitrification with both initial pH acidification and without acidification [49]. The initial pH was adjusted to 2 or 3 with HCl or H₂SO₄, and to 3 or 4 with CH₃COOH. In the solutions adjusted to an initial pH of 3 using CH₃COOH, or 2 using HCl, the bulk solution pH remained below 7, and no nitrate was detected after 15 h or after 8 h. However, when the pH was fixed to an initial value of 4 using CH₃COOH, or 3 using HCl, incomplete nitrate removal was observed. The pH, in this case, was higher than 10 after 24 h. Similarly, residual nitrate was detected after 24 h, when the initial pH was adjusted to 2 or 3 with H_2SO_4 . Therefore, the type of acid that is used for the pH control also affects the reaction. In particular, the authors ascribed the slowdown of denitrification when using H₂SO₄ to the generation of an excessive amount of H_2 , which accumulated on the surface of the Fe^0 and inhibited its corrosion and its reaction with nitrate [49]. Nevertheless, the worst condition was registered when the test was executed without acidification. Indeed, with an initial nitrate concentration of 100 mg NO_3^--N/L , and at an initial pH of 6.2, the residual nitrate was measured as 91 mg NO_3^- -N/L, and the pH was higher than 9.3, at the end of the experiment. Moreover, the reaction rate was slower than those of the tests that were terminated at acidic pH conditions [49].

However, the use of acids, such as HCl, H_2SO_4 , or CH_3COOH , to maintain the pH at acidic values entails high costs for the reagents. Furthermore, the use of these substances can alter the water quality because of the presence of chloride, sulphate, and acetate [50]. For this reason, during nitrate removal with Fe⁰ (10 µm), Ruangchainikom et al. supplied hydrogen ions by means of CO₂ bubbling [50]. The authors report an almost complete denitrification within 30 min of treatment, when treating a solution of 30 mg/L with

2 g/L of Fe⁰, and a CO₂ flowrate of 200 mL/min. During the tests, a variation in the pH was observed. The pH dropped from the original value of approximately 6.5 to about 3.5 in the first five minutes, and then increased again to 5–5.5, and became quite steady afterward [50]. This behaviour was explained by the consumption of hydrogen ions due to nitrate reduction (see Equations (1)–(5)) and to the production of hydroxide ions [50]. However, the CO₂ bubbling managed to maintain moderate acidic conditions.

The effects of the pH variation on the efficiencies were also studied by Ahn et al. [51]. The authors report that denitrification occurred for pHs between 4 and 7 [51]. Moreover, Huang et al. investigated chemical denitrification through Fe⁰ under unbuffered conditions [52]. The initial pH was equal to 7, and, within 24 h, a final pH of 9.4 was measured. Moreover, in this case, a nitrate removal lower than 10% was detected. Furthermore, the authors report that, after 24 h, the iron surface was coated with a black iron oxide. Other tests were conducted with an initial pH of 2.3. In this case, the denitrification process occurred in three stages. In the first 30 min, a rapid reduction in the nitrate concentration and a sharp increase in the pH (from 2.3 to 4.8) were observed. Afterwards, a slower rate of nitrate reduction was reported. In this phase, the pH increased from 4.8 to 6.2. A black coating on the Fe⁰ surface and a black precipitate, both identified as magnetite (Fe₃O₄), were observed at 5 and 10 h, respectively. Within 20 h, the pH reached a near neutral pH condition, and the remaining nitrate was removed [52].

In another study, nitrate reduction was explored by using a specific reactor that was designed to perform the experiments at a constant pH value (2, 2.5, 3, 3.5, 4, and 4.5) during the denitrification by Fe^{0} [53]. The authors report a rapid and complete reduction in the nitrate to ammonium under the acidic conditions tested. Furthermore, also in this case, the formation of a black coating on the Fe^{0} grains was observed (Figure 1) [53]. However, contrary to the findings of Huang et al. [52], the black coating was not identified as a commonly known iron oxide/hydroxide/oxide hydroxide or as green rust I/II. Furthermore, the black oxide was unstable, and it evolved with time into other oxides under certain conditions (Figure 1) [53].

The formation of iron corrosion compounds, in response to pH changes, has been investigated by other authors [54]. The experiments were conducted without pH control, after the first correction to 2, 3, or 4. The corrosion products detected were Fe_2O_3 , Fe_3O_4 (magnetite), and FeO(OH) (lepidocrocite). The presence of these compounds was found to change in response to the pH evolution. Indeed, in the test at the initial pH of 2, no lepidocrocite was detected. At a pH of 3, the FeO(OH) was about 7%, and it increased to 24% when the pH was increased to 4. When the initial pH was equal to 4, both magnetite and lepidocrocite were detected; however, after 24 h, the iron was covered with a black coat that consisted of magnetite. Therefore, the authors attributed the formation of FeO(OH) to the oxidation of the iron corrosion product by nitrate and to the initial existing dissolved oxygen (DO) in the presence of $Fe^{2+}_{(aq)}$. As the DO depleted and the environment became more reducing, the FeO(OH) was gradually transformed to Fe_3O_4 decreased.

The role of $\text{Fe}^{2+}_{(aq)}$ was also analyzed in another work [55]. With this aim, a first set of tests was conducted at pH values of 2.5 and 4.5, without adding Fe^{2+} ; the other experiments were conducted at a near neutral pH and an enhancing Fe^{2+} dosage. The results of the former tests, in accordance with other studies, confirm that low pH values are favorable for the process. However, when the pH was set to neutral values and the concentration of Fe^{2+} was increased, higher NO₃⁻ removal was observed. This behavior was ascribed to the capacity of the Fe^{2+} to facilitate the electron transfer from the Fe^0 core to the NO₃⁻. Furthermore, also in this case, the presence of magnetite and lepidocrocite on the exhausted material was revealed. In particular, Fe^0 particles were covered with an inner layer of Fe_3O_4 and an outer layer of γ -FeO(OH). The positive effect of Fe^{2+} is also confirmed by Xu et al., who added Fe^{2+} during denitrification through Fe^0 at a neutral pH [56]. Indeed, increasing removal yields were observed when the Fe^{2+} concentration was increased from 0 to 50 mg/L. However, by further increasing the concentration of Fe^{2+} , a lower efficiency



was detected, due to the agglomeration of Fe^{2+} , which acted as a colloid and lowered the reactivity of the Fe^0 [56].

Figure 1. SEM photographs of iron grains: (**a**,**b**) original surface conditions of uncoated Fe^0 (×1.2 k and ×10 k, respectively); (**c**) iron oxides starting to coat on the iron grain, picture taken after 5 min reaction with nitrate under the initial test conditions of 25 g uncoated $\text{Fe}^0/\text{L} + 2.14$ mM nitrate + pH of 2.5 (×20 k); (**d**,**e**) iron oxides fully coated on iron grains, picture taken after 30 min reaction (same conditions as (**c**), ×20 k); and (**f**) magnetite crystalline—a product of nitrate reduction by iron grains under near neutral pH (×20 k). This figure was published in: Huang, Y.H.; Zhang, T.C. Effects of low pH on nitrate reduction by iron powder. *Water Res.* **2004**, *38*, 2631–2642. Copyright Elsevier [53].

Since strongly acidic pH conditions were assessed to be the best for denitrification through Fe^0 , the experiments were initiated at a pH of 1.22 (which corresponds to 60 mmol H^+/L), 1.62 (24 mmol H^+/L), and 1.92 (12 mmol H^+/L), in the study of Zhang et al. [57]. At the pH of 1.62 and 1.92, the removal percentages were approximately 68 and 72%, respectively. Surprisingly, the experiment that was initiated at a pH of 1.22 yielded the lowest conversion (60%) of NO_3^- to NH_3 . To explain this behaviour, the authors hypothesised the existence of a lower pH threshold, below which the denitrification efficiencies decrease [57].

However, a more recent study explored the possibility of operating at higher values of pH [58]. In this case, ZVI powder (0.147-0.125 mm) was pretreated with H_2O_2/HCl

(named prtZVI) under both argon and air exposure to improve its efficiency. The authors report a complete nitrate removal (96.0–100%) in 180 min of treatment for the initial pH values, which ranged between 4 and 7. However, an efficiency of 81.8% was reported at a pH of 8, and a considerable denitrification for pHs higher than 9 occurred. These results, which are different from all the findings of the abovementioned works, are ascribed to the increased reducing power of the of prtZVI system.

The possibility of operating at higher pH values is a profitable aspect. Indeed, the continuous use of acids to maintain acidic pH conditions involves costs. Therefore, other techniques to achieve efficiencies that are comparable to those obtained under strong acidic conditions can be tested. The use of CO_2 bubbling to supply hydrogen produced satisfactory removal yields. Furthermore, the pretreatment of iron powder with H_2O_2 and HCl allows the performance of the denitrification without pH control, and at a pH higher than 7.

2.1.2. Effect of Dissolved Oxygen

The presence of dissolved oxygen (DO) can have negative effects on denitrification through ZVI. Indeed, oxygen may compete for electrons, which reduces the number of agents or reactive sites on the iron particles [18]. Furthermore, oxygen can also produce iron corrosion products, which could lead to surface passivation phenomena [18]. To avoid the inhibition of denitrification, several studies have been conducted under anoxic conditions, by purging the solution with nitrogen gas [16,47,57] or argon gas [49,52,53]. On the other hand, some works were performed under oxic conditions to assess the effect of the DO on the denitrification process performance [58–64].

Yang et al. investigated the effect of the storage time and air exposure on the nitrate reduction performance for a system comprised of iron pretreated with H_2O_2/HCl (prtZVI) and an aqueous nitrate solution (20 mg NO_3^--N/L) [58]. While 7-day storage resulted in a slight improvement in the reduction efficiency, the prolonged storage time (up to 30 days) did not provide further enhancement of the efficiency under anoxic conditions. This slight improvement was attributed to the possible transformation of the Fe³⁺ to magnetite by adsorbing Fe²⁺, or through the reaction with Fe⁰. Air exposure caused a slight deterioration in the nitrate removal performance over argon. This reduction in the denitrification performance was elucidated by the electron competition that was induced by the DO and the generation of a passive film [58].

However, Huang and Zhang suggest that oxygen did not influence denitrification by Fe⁰ when used together with dissolved Fe²⁺ [59]. Indeed, when utilizing both magnetitecoated Fe⁰ and uncoated Fe⁰ to treat a 100 mg/L nitrate solution, in the presence of Fe²⁺_(aq), no differences were noticed in the gradual reduction in the Fe²⁺, in the stable increase in the pH, or in the formation of a large quantity of black precipitate, with or without O₂. However, the formation of a brownish precipitate was observed during the first 2 h of the test conducted with O_2 . This brownish precipitate was presumably lepidocrocite (γ -FeOOH), while the black precipitate was magnetite (Fe₃O₄). On the basis of the twolayer semiconductor model, the coating of oxide formed on the iron surface is composed of an inner layer of magnetite and an outer layer of magnetite or lepidocrocite [59]. It was observed that electrons can migrate more easily in the magnetite layer than in the maghemite or lepidocrocite coating [59]. Therefore, the outer layer of oxide may reduce the iron reactivity. The formation of magnetite mainly occurred in the absence of DO, while lepidocrocite was the oxidation product that was observed in the presence of oxygen [59]. Hence, in the presence of DO, the formation of lepidocrocite may hinder the nitrate reduction. However, the authors observed similar efficiencies in the presence and absence of O_2 . This result is ascribed to the presence of Fe^{2+} in the solution, which seemed to revitalize the oxide shell and promote the Fe⁰ reactivity. In effect, this was confirmed by a control test, in which Fe^{2+} was not added to the solution, and in which a decrease in the efficiencies was observed. The formation of lepidocrocite in the presence of DO is also reported by Xiaomeng et al. and Suzuki et al. [54,55]. However, Xiaomeng et al. ascribe the

formation of lepidocrocite to both DO and Fe²⁺; whereas Huang and Zhang assume that the compound was formed by the sole presence of DO and not Fe²⁺, since it was found with and without the addition of Fe²⁺_(aq) to the solution [54,59].

Nevertheless, according to other works, dissolved oxygen may also have a positive impact on the denitrification process. Indeed, it was hypothesized that DO could enhance nitrate reduction through the production of more reducers, such as dissolved or surface-bound Fe^{2+} [18]. In effect, satisfactory results have been reported in the presence of oxygen [60,61,64].

Lee et al. used microscale zero-valent iron (100-300 mesh) to perform denitrification under oxic conditions in both batch and continuous systems [60]. The batch tests showed a removal yield of 97.6% and a conversion to ammonium nitrogen of 35.2%, after 2 h of treatment, with an initial concentration of 25 mg NO_3^3 -N/L, and by using 300 mesh ZVI in a concentration of 2 g/L and at a pH of 2. The main end product was found to be nitrogen gas, which is a desirable product as it is harmless. Iron (hydr)oxides were formed during the reaction with nitrate, oxygen, and hydroxyl ions. Furthermore, a higher presence of oxygen and a lower content of iron were detected for the tests at a pH of 3. The authors ascribe this fact to the formation of more iron (hydr)oxides, which is due to the enhancement of the iron dissolution at a low pH and the increase in the Fe²⁺ in the bulk solution. The main corrosion product that was detected under oxic conditions was hematite. The effectiveness of ZVI under oxic conditions was also confirmed by the continuous tests, which were performed with a horizontal flow reactor that was filled with ZVI and sand. Indeed, a long-term continuous application (1700 h) yielded satisfactorily nitrate removal efficiencies that varied between 88 and 100%. The conversion of nitrate to ammonium was 30% after 500 h, and 10% after 1700 h [60].

Westerhoff and James also report an improvement in the process performance that is due to the presence of DO [61]. Packed column experiments were conducted, with an influent groundwater that was characterised by a DO of 8–8.5 mg/L, a pH of 8.3–8.5, and a nitrate concentration of 25 mg NO_3^- -N/L. It was found that the lower initial DO resulted in 50% less reduction in the nitrate, while increasing the initial DO concentrations led to an increased percentage of nitrate removal.

In the relevant literature, the formation of some reducers, such as green rust, was also reported in the presence of oxygen. Indeed, green rust was demonstrated to reduce nitrate to ammonium [62,63]. As these compounds are unstable, their impacts are considered to be minor in a typical batch experiment. On the other hand, in a packed column, the precipitates could have more influence on the process performance. Furthermore, with this configuration, a continuous loading of DO is provided, which allows modifications of the Fe⁰ surface or precipitates to form.

The positive effect of DO on the denitrification process performance is also confirmed by the work of Guo et al. [64]. Their experiments were initiated in a wide range of initial pHs that varied from 2 to 11 in the presence of oxygen, and they used an initial nitrate concentration of 14 mg N/L and an iron powder dose of 0.05 g per 10 mL of sample. For comparison, experiments in the absence of oxygen were also performed. The authors report negligible nitrate reduction in the absence of O₂ at a pH higher than 5. On the other hand, a noticeable reduction in the nitrate in the initial pH range (from 1 to 8) was obtained under oxic conditions owing to the iron corrosion that took place through anodic Fe⁰ dissolution and cathodic oxygen reduction. Nevertheless, a clear trend of a decrease in the reduction efficiency with increasing pH was also reported and explained by the negative role of the oxygen-derived corrosion products on the iron dissolution rate [64].

2.1.3. Effect of Initial Nitrate Concentration

The initial nitrate concentration also influences the denitrification process performance. Therefore, in the literature, various values of the initial nitrate concentration were investigated. Huang et al. tested the removal of nitrate by ZVI in the initial concentration range of 50–500 mg/L of NO_3^- [16]. For concentrations up to 300 mg/L, the denitrification

was complete within 1 h. However, at higher concentrations, the reaction rate reduced rapidly in the first 20 min, and there was still residual nitrate after 1 h of treatment. The dependence of the reaction rate on the nitrate concentration was interpreted through an apparent reaction order of 1.7, with respect to the nitrate concentration.

Similar data were reported by Zhang et al., who studied the effect of the initial concentration by considering solutions with 12.5, 25, and 100 mg/L of NO_3^- -N [57]. The concentration of the zero-valent iron was 0.416 g/L, which corresponds to molar ratios between the reactive material and the pollutant of 8.33, 4.16, and 1.04 molFe/molN, respectively. After 120 min, the nitrate removal yields were 94, 72, and 29%, respectively, which corresponds to a significant reduction in the removal efficiency with increasing concentrations.

Siantar et al. used zero-valent iron to treat solutions with concentrations of 0.0566 g/L, 0.51 g/L, and 2.73 g/L of NO_3^- -N [65]. A complete denitrification was obtained within 14 min for the solution with 0.0566 g/L of nitrate, while an efficiency of only 5% was detected with 2.73 g/L. The test conducted with 0.51 g NO_3^- -N/L yielded a 76% nitrate removal after 16 min. The authors attributed this decrease in efficiency to the reduced intermediates, which competed with the NO_3^- for reactive sites.

Cho et al. prepared Ca–alginate beads (FMAB), entrapping a mixture of Fe⁰ and magnetite to achieve denitrification, and they tested groundwater samples with various initial nitrate concentrations (2.19, 4.38, 8.02, and 10.16 mM) [45]. After 48 h of treatment, a decrease in the removal yields with the increasing initial nitrate concentrations was observed. This result is ascribed to the increased competition for a limited number of reaction sites at the FMAB. However, the authors also observed an improvement in the overall nitrate removal from 1.11 to 3.51 mM, with an increase in the initial nitrate concentration from 2.19 to 10.16 mM. Therefore, the FMAB was found to maintain its reactivity at a high nitrate level.

Contrary to the aforementioned data, some studies report an enhancement in the denitrification performance with increasing initial nitrate concentrations [47,61]. Hao et al., for example, report a decrease of the abatements when the nitrate concentration was decreased from 100 to 50 and 25 mg/L [47]. Moreover, Westerhoff and James, when testing both iron filings and iron chips in continuous-flow packed bed columns, reported increased nitrate removal rates with increasing initial nitrate concentrations, but by different extents for the two Fe⁰ materials [61].

The kinetic study of Xiaomeng et al. indicates that a pseudo-first-order law well described the dependence of the reaction on the nitrate concentration, and the observed reaction rate constant (which ranged from 0.0334 to 0.0361 1/min) was independent of the initial nitrate concentration [54]. Indeed, after 120 min of reaction, an almost complete denitrification was observed for all the nitrate concentrations between 50 and 400 mg/L.

Therefore, the initial concentration of nitrate can have different impacts on the process. High nitrate concentrations may create a higher concentration gradient, which enhances the diffusion of the contaminant on the surface of the material and, thus, promotes the reaction. On the other hand, a high amount of nitrate implies a higher consumption of the reactive material, which leads to a decrease in the efficiencies. In effect, this process also depends on the quantity of Fe^0 that is loaded, since, at higher amounts of reactive material, for a given nitrate concentration, the process performances may be improved.

2.1.4. Effect of Temperature

The denitrification process through microscopic zero-valent iron is enhanced with increasing temperatures [66–69]. Ahn et al. tested the nitrate reduction by zero-valent iron at elevated temperatures through batch and column experiments [66]. Under both conditions, the increase in the temperature produced increased removal rates. In the batch experiments, a pseudo-first-order law was found to simulate the data. The rate constants, under unbuffered and buffered conditions at 75 °C, exceeded, by 5 and 19 times, respectively, the rate constants at 20 °C. These results were also confirmed by the tests that were conducted in the column system. Indeed, the extent of the nitrate reduction was slow and

incomplete in the unbuffered solution at room temperature, while an abatement of 88% was found after only 30 min at 50 °C. At 75 °C, the nitrate was completely removed after 30 min. Furthermore, at a pH of 7.4, with 0.1 M of the HEPES [N-(2-hydroxyethyl)piperazine-N'-(ethanesulfonic acid)] buffer, the abatement after 30 min was increased from 91.4 to 100% when the temperature was elevated from 20 to 50 °C. After only five minutes of treatment, a removal percentage of 88% was determined at 75 °C [66]. In another study, the removal of nitrate and ammonium from livestock wastewater by using HCl-treated Fe⁰ hybrid systems was explored [67]. The experiments were conducted at 15, 25, and 45 °C, and an enhancement of the removal rates was observed for all the hybrid systems tested when the temperature was increased. This result was ascribed to the increase in the available heat energy, which was high enough to overcome the activation energy barrier for nitrate reduction at a high temperature [67]. In effect, several mechanisms are involved in the nitrate removal process through Fe⁰, such as diffusion, adsorption onto the iron surface, and the chemical reduction of nitrate [18]. The limiting step of the process can be estimated by calculating the activation energy (E_a) [18]. Indeed, the diffusion process should require less energy than the chemical reduction [68]. Liou et al. performed nitrate reduction by using pretreated zero-valent iron, the surface of which was heated to 400 $^{\circ}$ C with hydrogen gas [68]. The experiments were conducted in the range of temperatures that varied between 10 and 45 °C. The authors found that the observed kinetic constants for the process showed a temperature dependence that was consistent with the Arrhenius equation. The values of the activation energy, which were calculated from this equation, proved that the chemical reaction, rather than diffusion, controlled the rate of the nitrate removal [68]. This result was also confirmed by the findings of the same authors, who used Fe^{0} for the nitrate removal at temperatures between 10 and 60 °C [69]. The activation energy was calculated as 42.5 kJ/mol, which indicates a process that is controlled by the chemical reaction step, since a typical mass-transport-controlled reaction in water is characterised by $E_a = 10-20 \text{ kJ/mol}$ [69].

2.1.5. Effect of Dissolved Ions

Polluted water and groundwater are often characterised by the simultaneous existence of various contaminants. When more than one substance is present in the solution, different mechanisms may take place. Indeed, these compounds may compete with nitrate ions for reactive sites and may thus cause a lower denitrification. In other cases, instead, the reactivity of Fe^0 can be improved by these substances, which leads to a greater removal of nitrates. In some of the literature works, the influence of other ions on the process was analyzed. The effect of Cl^- was studied by Huang et al. by adding 1000 mg/L of Cl^- (as NaCl) to a solution of 30 mg/L of NO_3^- -N treated with 5% magnetite-coated Fe⁰ [16]. Although it was hypothesized that there would be a greater corrosion of the Fe⁰ and, thus, an enhanced nitrate removal, the chloride did not contribute to the improvement of the chemical denitrification. Indeed, an abatement lower than 10% was detected after 72 h of treatment [16]. Nevertheless, the enhanced corrosion of the Fe⁰ surface and the increased surface reactivity was proven in another study [50]. Indeed, increasing nitrate removals were achieved when increasing concentrations of NaCl (35.5, 106.5, and 213 mg Cl^{-}/L) were tested [50]. However, the authors report a limitation of the nitrate reduction at the highest chloride concentrations [50].

The impact of phosphate on the process was also studied by other authors [60,66]. Lee et al. examined the effects of the PO_4^{3-} -P concentration, which ranged between 20 and 70 mg/L, during the treatment of a nitrate solution of 25 mg/L with 2 g/L of Fe⁰ [60]. The process improved at 20 mg/L of PO_4^{3-} -P, while it was not influenced at 30 mg/L and was inhibited at 70 mg/L [60]. This result was ascribed to the competition of nitrate and phosphate for the same reactive sites [60]. The authors also observed increased N₂ selectivity when the phosphate concentration was higher. This was attributed to the promotion of the electron transfer by PO_4^{3-} [60]. Finally, because of the insignificant decrease in the PO_4^{3-} -P concentration during 1 hour of treatment, a better affinity of nitrate

than phosphate to the iron surface was supposed [60]. On the contrary, Ahn et al. report a negative impact of phosphate on denitrification [51]. Indeed, while conducting the nitrate removal in a phosphate buffer, the authors found that the nitrate was not reduced by iron, while the phosphate concentration decreased [51]. In this case, the formation of $Fe_3(PO_4)_2$ on the iron surface was supposed, which inhibited the reaction with nitrate [51].

2.2. Nanoscopic Iron

Nanoscale iron particles are sub-micrometric particles (Figure 2) [69] that are characterised by dimensions of 1–100 nm [44]. The reduced size confers on the material a higher specific surface area and, thus, higher reactivity, compared to the other types of ZVI [44]. For these reasons, nZVI has been increasingly exploited to treat nitrate-polluted waters [70]. As for microscopic Fe⁰, the denitrification through nZVI is also affected by various operating parameters.



Figure 2. Transmission electron microscopy image of fresh nano-Fe⁰ particles. This figure was published in: Liou, Y.H.; Lo, S.L.; Lin, C.J.; Kuan, W.H.; Weng, S.C. Chemical reduction of an unbuffered nitrate solution using catalyzed and uncatalyzed nanoscale iron particles. *J. Hazard. Mater.* **2005**, *127*, 102–110. Copyright Elsevier [69].

2.2.1. Synthesis of Nanoscopic Zero-Valent Iron

Iron nanoparticles are produced by the reduction of ferric ion by borohydride, according to the following reaction [70–73]:

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 + 3H_2BO_3^- + 12H^+ + 6H_2$$
(8)

In the traditional method, nZVI is synthesised by adding a sodium borohydride solution (NaBH₄) dropwise to a solution of ferric chloride (FeCl₃·6H₂O) at room temperature and under magnetic stirring [70–73]. Borohydride is generally added in excess of the stoichiometric dose (Fe/BH₄: 4 mol/3 mol) to achieve the fast and complete reduction of Fe³⁺ to Fe⁰ [71]. For instance, Lien et al. applied a 1:1 volume ratio between NaBH₄ 0.25 M and FeCl₃·6H₂O 0.045 M [71]. Therefore, the ratio between borohydride and iron was 7.4 times higher than the molar ratio that was calculated from Equation (8). Once the borohydride solution is completely added to the ferric chloride solution, the mixture is centrifuged, and the recovered precipitate is washed with distilled water and is used for the experiments [70,73].

The method described above was modified in some works in order to improve the reactivity of nZVI [74–77].

Ghosh et al. followed the traditional chemical reduction method, but they exploited three different alcohols (ethanol, ethylene glycol, and glycerol), along with water, as the reaction medium to synthesize Fe⁰ nanoparticles [74]. Three types of well-dispersed single-phasic flower-like zero-valent iron nanoparticles were produced by their modified process [74].

Moreover, Liou et al. prepared three different types of nZVI by using three concentrations of the precursor FeCl₃·6H₂O that were equal to 1, 0.1, and 0.01 M [75]. The material that was produced by using 0.01 M of iron chloride was characterised by the smallest particle size (equal to 9–10 nm) and the greatest surface area (56.67 m²/g). This led to a higher reactivity of the material, compared to the iron that was produced with 1 and 0.1 M of iron chloride [75].

The effects of several variables during the production of the nanoparticles, such as the concentration, the delivery rate, the liquid volume of sodium borohydride, the precursor concentration (FeCl₃), the reaction temperature, the mixing speed, the pH, and the aging time, were investigated in order to find the optimum conditions [76]. For the NaBH₄, the optimal settings were a concentration of 16 g/L, a feeding rate of 40 mL/min, and a liquid volume of 120 mL. Moreover, a reaction aging time of 5 min, a mixing speed of 500 rpm, and a pH of 6 improved the nZVI reactivity [76]. Increasing the reaction temperature resulted in a decrease in the average particle size, and the highest reactivity was achieved at 90 °C. As is also reported by Liou et al., a low concentration of the precursor improved the nZVI reactivity. In this case, the highest efficiency was gained at 20 mg/L of FeCl₃ [76].

The green synthesis of nZVI for nitrate removal was also performed [77]. In this case, green tea (GT-Fe) and eucalyptus (EL-Fe) leaf extracts were used as reducing agents instead of NaBH₄. Indeed, the extracts from the dry leaves of the two plants were added to a solution of FeSO₄, and the mixture was stirred for 30 min to reduce the Fe²⁺ to Fe⁰. The nanoparticles were filtered, washed with ethanol, dried under vacuum at 50 °C for 12 h, and kept in a N₂ atmosphere prior to use. The GT-Fe and EL-Fe nanoparticles resulted in the less effective removal of the nitrate than the nZVI produced by the traditional chemical method. However, the green-synthesised nZVI exhibited strong stability, even after being aged in air for two months, where the removal efficiency of the nZVI dropped to around 50%, while the GT-Fe and EL-Fe nanoparticles remained almost the same [77].

Different types of reagents were also tested to reduce the aggregation phenomena that can occur among iron nanoparticles [78–81]. For this purpose, poly(1-vinylpyrrolidone-co-vinyl acetate) (PVP/VA) was used as a stabilizer of nZVI during the production of the material [78]. In particular, PVP/VA was added to a FeCl₃ solution and was mixed under a nitrogen purging condition for 30 min, and then, the NaBH₄ was added dropwise to realize the Fe³⁺ reduction [78]. However, the reactivity of the PVP/VA-coated nZVI was lower than that of bare nZVI. This was attributed to the decreased reactive sites on the synthesized nZVI surface as a result of the ineffective surface coating [78].

Wang et al. [79] prepared a higher-surface-area spherical nanoscale zero-valent iron (HNZVI) cluster by using ferrous sulphate (FeSO₄·H₂O) as a precursor and KBH₄ as a reducing agent, in the presence of a dispersion agent of polyglycol (PEG), in a mixture of water and ethanol. The prepared nanoparticles were characterised by a dimension of 80 nm and a specific surface area of 54.25 m²/g [79].

A mixture of two environmentally friendly surfactants (sorbitan monooleate (Span 80) and polyoxyethylene (20) sorbitan monostearate (Tween 60)) was used as the stabilizer agent during the synthesis of nZVI through the reduction of $FeSO_4$ by KBH_4 [80,81]. Nanoparticles with dimensions of 80–90 nm were obtained by this application [80,81].

Except for chemical reduction, some innovative methods have also been developed to produce nanoscopic iron particles [82–84].

Chen et al. combined electrochemical and ultrasonic methods to synthesise iron nanoparticles through the electroplating of iron particles [82]. In particular, FeCl₃ was used as the precursor, and a platinum cathode was utilized for the production of the nZVI particles. The iron particles were removed from the cathode with ultrasonic vibrators at

20 kHz. The produced particles had a diameter between 1 and 20 nm, and a specific surface area of $25.4 \text{ m}^2/\text{g}$ [82].

To increase the efficiency of nZVI, Kassaee et al. developed a modified arc discharge technique for the synthesis of zero-valent iron nanoparticles [83]. nZVI iron was synthesised by applying a current of 50 A/cm² to two iron electrodes that were submerged in water until an explosion occurred. The nanoparticles derived from this process had a dimension of 37 nm. The authors report a denitrification efficiency of the nZVI produced through arc discharge that was twice that of the iron nanoparticles produced through the traditional reduction method. Furthermore, the nZVI fabricated by arc discharge that resulted were free from extraneous impurities, as no chemicals were used in their preparation [83].

Liu et al. prepared two types of nZVI by the hydrogen reduction of natural goethite (NZVI-N) and hydrothermal goethite (NZVI-H) [84]. NZVI-N was produced by installing 10 g of crushed natural goethite into a quartz tube under different temperatures, and a hydrogen flowrate of 100 mL/min derived from the hydrogen generator for 6 h. Hydrothermal goethite was created by the hydrothermal synthesis of ferric nitrate. NZVI-H was then prepared by applying the same procedure followed for the NZVI-N to hydrothermal goethite. However, in this case, the hydrogen generator was not turned off until the temperature of the furnace decreased to room temperature [84].

The coating of the nZVI with another metal was also tested [85–87]. Vilardi and Di Palma coated iron nanoparticles with copper, and they used this bimetallic compound for the removal of nitrate [85]. The authors report a remarkable enhancement in the nitrate removal that was mediated by the bimetallic nanoparticles, in comparison with the use of bare nZVI. In particular, a higher nitrate removal was obtained by using 0.05 g/L of Cu/Fe nanoparticles, with respect to the use of a double concentration (0.1 g/L) of bare nZVI [85]. Nano-Fe/Cu bimetallic particles were also used by other authors for nitrate removal in a multilayer system through an up-flow packed sand column [86]. In this case, also, the nano-Fe/Cu particles exhibited a more efficient and rapid nitrate removal than nZVI when the feed solution was simulated groundwater [86]. In another work, nZVI particles were doped with Cu, Ag, and Au [87]. The highest nitrate reduction efficiency (equal to 77%) and the lowest nitrite yield ratio were achieved with nZVI–Au particles [87].

2.2.2. Effect of pH

The removal of nitrate by means of nZVI is often reported to be dependent on the pH (Table 1). Chen et al. tested nitrate removal considering a concentration of 20 mg/L in the pH range of 4–7, by using 0.5 g/L of nanoscale zero-valent iron that was produced by combining electrochemical and ultrasonic methods [82]. The nitrate removal efficiencies varied between 60 and 78%, and a faster nitrate decline and more reduction in terms of the g NO₃⁻-N/g nZVI were observed at lower pHs. Furthermore, a first-order law was found to simulate the reaction and kinetic coefficients for the four pH values, which were directly related to pHs with $R^2 > 0.95$. This finding was also confirmed by the results of another work, in which 100 mg/L of nitrate was treated by exploiting 2 g/L of nZVI at a pH between 2 and 5 [76]. The authors report an abatement of about 80% after 60 min of reaction at a pH of 5, while a complete removal was attained after 30 min at a pH of 4, and at lower pHs. Furthermore, a test without pH control was also performed, which resulted in only a 40% removal after 60 min of treatment. This result was ascribed to the increase in the pH to 7.6. Indeed, the authors state that, at an acidic pH, the ferrous hydroxide and other protective layers at the surface of nano-sized ZVI are dissolved, which yields more fresh reactive sites for the chemical reduction of nitrate [76]. Similar results are reported in another work, in which the reduction of 100 mg/L of nitrate by using nZVI at initial pHs of 1.5, 7, and 9 was tested [88]. Indeed, a greater performance of the nZVI in acidic pH conditions compared to neutral conditions was observed. Moreover, the nZVI presented the lowest kinetic performance in the alkaline medium.

Other authors, who used 0.5 g/L of nZVI to treat solutions with 50 mg/L of nitrate, observed a slight improvement in the nitrate removal and ammonia generation when

the pH decreased from 7 to 3 [89]. A minor decrease in the process performances with increasing pH was also observed by Siciliano [70], when using nZVI in concentrations that changed between 1 and 5 g/L, to treat solutions with 50, 70, and 95 mg/L of nitrate at pHs of 3, 5, and uncontrolled. The increase in the pH from 3 to 5 produced a relatively significant abatement reduction only for the highest nitrate concentrations that were tested. In the tests that were conducted at uncontrolled pH, the bulk solution pH increased from about 5.9, 5.6, and 5.4, respectively, to values higher than 9, in a few minutes. Although the removal yields were lower than those observed at pHs of 3 and 5, notable nitrate reductions were still achieved at uncontrolled pH. This result was ascribed to the capacity of iron corrosion products to achieve appreciable nitrate reduction [70].

In other cases, a poor or negligible effect of the pH on the process performance was observed. Wang et al. synthesized a higher-surface-area spherical nanoscale zero-valentiron (HNZVI) cluster [79]. By using HNZVI at the initial pHs of 3, 5, and 7, the authors found that, although the efficiency increased as the pH decreased, the effects of the pH on the removal rate of the nitrate diminished rapidly, especially at high nanoscale iron concentrations. Furthermore, a test without pH control was also performed, and the efficiency after 30 min was the same as that obtained at the initial pHs of 3, 5, and 7. Similarly, Ryu et al., who applied various types of nZVI to treat solutions with initial nitrate concentration of 1000 ppm, and without correcting the pH, state that nitrate reduction could successfully occur without pH control [90]. Moreover, in another work, 0.25 g of nZVI, which was synthesized by a modified microemulsion system by using nonionic surfactants were added to 125 mL of nitrate solution, with a concentration of 80 mg/L, for the denitrification performed at the initial neutral condition without pH control [80,81]. The authors report a complete denitrification, which was achieved in 30 min of treatment [80,81]. Moreover, another work was conducted at uncontrolled pH at different iron doses (0.2, 0.35, 0.5, and 1 g) with 50 ppm of nitrate [91]. A rapid increase in the pH to 9–10, within a few minutes after the beginning of the reaction, was observed. Although the pH remained between 9 and 10 for each iron dose, the authors report a rapid reduction in the nitrate [91]. A rapid increase in the pH was also reported by Liou et al. [75] when testing the removal of 40 mg/L of nitrate without pH control by using 0.0265 g of Fe^0 . However, in this case, the denitrification was not complete, and the main reaction product was ammonium [75].

Considering the studies analysed in the present section, it can be concluded that the pH has a crucial role in denitrification by means of nanoscopic iron. As for mZVI, in most cases, acidic pH enhanced the process performances. However, as is evident in Table 1, when using nZVI, satisfactory removal yields can be achieved under both acidic and slightly alkaline environments, and even under uncontrolled pH conditions. This can be attributed to the reduction or adsorption capacity of the corrosion compounds that are formed under alkaline conditions on the surface of nZVI. These products, indeed, may have greater specific surface areas than the compounds that are produced by the corrosion of microscopic iron. Furthermore, the different procedures of synthesis of the nZVI could also affect the efficiencies. In fact, some preparation methods could generate more reactive nanoparticles, which are able to obtain satisfactory removal yields, even at alkaline pHs. Obviously, the capacity of reducing nitrate also at alkaline pH is a profitable characteristic of nZVI, as it reduces the costs of adding acids or of using buffer solutions.

ZVI Size	ZVI (g/L)	N-NO ₃ ⁻ (mg/L)	T (°C)	Oxygenated Conditions	pН	Efficiency (%)	Main Reaction Products	Refs.
6–10 μm	20	50 *	25	anaerobic	2 ** >4 **	95 negligible	NH ₃	[16]
iron filings	100	45 *	25	anaerobic	2.5 ** 4 **	80 <10	NH_4^+	[47]
100 mesh	33	100	22	anaerobic	2 ** 4 **	100 <40	$\rm NH_3/\rm NH_4^+$	[49]
0.5 mm	50	30	24 ± 1	anaerobic	2.3 ** 7.1 **	98 <10	NH_4^+	[52]
0.5 mm 160–200 mesh	25 20	30 50	25 20–22	anaerobic aerobic	2 and 3 2 **	100 100	NH_4^+	[53] [54]
20–60 mesh	1000	30	24 ± 1	aerobic	2.5 ** 4.5 **	100 50	NH_4^+	[55]
1.5 μm	0.416	25	20	anaerobic	1.62 ** 1.92 **	68 72	NH ₃	[57]
0.147–0.125 mm	4	20	20 ± 1	anaerobic	<8 ** 8 **	96–100 81.8	NH_4^+	[58]
iron powder	6.25	73 *	25	anaerobic	4.7 ** 7 **	100 0	NH_4^+	[51]
1–20 nm	0.5	20	25	anaerobic	4 7	78 60	N_2 , NH_4^+	[82]
50–80 nm	2	100	25	aerobic	${\leq}4$ 5	100 80	NH_4^+	[92]
1–100 nm	5	95	20	aerobic	3 5 uncon	99.9 73.1 63	NH_4^+	[70]
80 nm (iron cluster) <10 nm (nanoparticles)	4	80	25	aerobic	3 ** 5 ** 7 **	100 100 100 100	NH_4^+	[79]
80–90 nm	2	80	25	anaerobic	7 **	100	NH_4^+	[81]

Table 1. Effects of pH on nitrate removal efficiencies with mZVI and nZVI.

* concentration expressed in terms of NO_3^- ; ** initial pH; uncon: uncontrolled.

2.2.3. Effect of Dissolved Oxygen

As mentioned in Section 2.1.2, dissolved oxygen may hinder the denitrification process because it competes for electrons and reactive sites and causes surface passivation phenomena, or it can enhance the nitrate reduction through the production of more reducers [18]. Khalil et al. [88] report that the abatements were reduced by 40% at the equilibrium state through confrontation with anoxic and aerobic conditions. Moreover, Wang et al. [79] observed a reduction in the denitrification efficiencies of the higher-surface-area spherical nanoscale zero-valent iron (HNZVI) cluster by passing from a closed to an open system. Indeed, by using 1 g/L of iron, 95% of the nitrate was reduced in the closed system, and 90% of the nitrate was removed in the open system after 30 days. This difference in the removal efficiency is explained by the role of the electron acceptor that is assumed by oxygen under aerobic conditions. In particular, the reducing capacity of nanoscale iron decreased along with the consumption of HNZVI, the production of insoluble compounds, and the re-aggregation of nanoclusters [79]. Because of the continuous dissolving of the oxygen in the open system, the HNZVI was probably deactivated by the formation of an iron oxide film [79]. However, the decrease in the efficiencies that was obtained by passing from a closed to an open system was moderate.

On the other hand, some studies report an oxygen consumption during the first minutes of treatment that reduced the possible negative effects of DO. Yang and Lee [92] state that the electron-consuming effect that is due to DO was overcome by the strong electron-donating capacity of nZVI particles, almost during the entire treatment. Indeed,

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the DO concentration decreased from about 6 mg/L to below 1 mg/L within the first 5 min of treatment. Therefore, the DO acted as an electron acceptor in the very first few minutes of the reaction [92]. Considering the low DO concentrations that were detected at the end of the process, the system could be considered almost anoxic. Similarly, other authors observed a very fast decrease in the DO, which was faster than the reduction in the nitrate concentration [82]. Therefore, the system was considered anoxic, except at the very beginning.

2.2.4. Effect of Initial Nitrate Concentration

The efficiency of nanoscopic zero-valent iron is also affected by the initial concentration of nitrate. Solutions with nitrate concentrations of 50, 100, 200, 300, and 500 mg/L were treated with nZVI in the presence of $CuCl_2$ [88]. For the initial concentrations of 50, 100, and 200 mg/L, the nitrate was completely removed in 5, 20, and 30 min, respectively. When the initial concentration was 300 mg/L, it took 60 min to remove all the nitrates. Finally, for the concentration of 500 mg/L, there was still residual nitrate after 100 min of treatment. In another work, at uncontrolled pH, the tests conducted by treating 50, 70, and 95 mg/L of nitrate with 5 g/L of nZVI, after 1 h, showed removal yields of 98, 87.1, and 63%, respectively [70]. The process followed a first-order kinetic with respect to the nitrate concentration, and the observed kinetic constants increased with the ratio between the iron and the initial nitrate [70].

However, Zhang et al. [93], by treating solutions at various initial nitrate concentration through nZVI at neutral pH conditions, report final removal efficiencies for different concentrations that are close to each other. The absolute removal amount increased with the increase in the initial nitrate concentration. In particular, with initial nitrate concentrations of 20, 30, 40, and 50 mg/L, the removal yields were, respectively, equal to 96.1, 96.2, 97.2, and 96.5% after 1 hour of treatment [93]. The process was described with a pseudo-firstorder reaction with respect to the nitrate concentration, and the kinetic constants varied between 0.0851 and 0.0865 1/min at the various tested initial concentrations. Therefore, the observed reaction rate constant was found to be independent of the initial nitrate concentration within the considered concentration range [93]. Similar results were obtained by Liu et al., who exploited two types of nZVI that were prepared, respectively, by the hydrogen reduction of natural goethite (NZVI-N), and by hydrothermal goethite (NZVI-H), for the denitrification of solutions with nitrate concentrations of 20, 40, 60, 80, 100, and 120 mg/L [84]. With both the materials, an increase in the nitrate removal rate with increasing nitrate concentrations was observed, which was due to the enhancement of the reaction probability between the iron and nitrate. Furthermore, by comparing NZVI-N and NZVI-H, the latter showed a decrease in reactivity in a short time because of the formation of iron oxide and hydroxide on the surface of the iron [84]. When the synthesised well-dispersed single-phasic flower-like zero-valent iron nanoparticles were applied to aqueous nitrate solutions (10–400 mg/L), an almost complete denitrification was achieved for each concentration within 120 min [74].

The results that were obtained with nanoscopic zero-valent iron are similar to the findings that were obtained for zero-valent iron in the microscopic form. Indeed, as already expressed for mZVI, the initial concentration of the pollutant can have different effects on the removal process. Therefore, also with nZVI, in some cases, the increase in the nitrate concentration caused a decrease in the efficiencies, which was probably due to the higher consumption of the reactive material. However, in other cases, the authors report satisfactory removal yields at high nitrate concentrations. This finding, which is also mentioned in Section 2.1.3, may be ascribed to a greater concentration gradient, which improves the diffusion of nitrates on the surfaces of nanoparticles, thereby enhancing the efficiencies. Furthermore, as explained by Liu et al. [84], the higher the nitrate concentration, the greater the probability of a reaction between the nitrate and the iron.

2.2.5. Effect of Temperature

The denitrification process by nZVI appeared to be positively influenced by temperature [18]. By increasing the temperature from 30 to 50 °C, the nitrate removal was enhanced from 67.6 to 96.2% after 10 min [94]. Furthermore, Liou et al. [68] considered four process temperatures, which were equal to 10, 25, 40, and 60 °C. The rates of the nitrate reduction exhibited temperature dependencies that are consistent with the Arrhenius equation. The kinetic constants that were calculated with this law, at 10, 25, 40, and 60 °C, were equal to 0.75, 1.37, 1.66, and $4.26 \times 10^{-2} \text{ min}^{-1}$, respectively [68]. The activation energy that was determined from these data was 25.8 kJ/mol. As was already mentioned in Section 2.1.4, the activation energy of a typical mass-transport-controlled reaction is 10–20 kJ/mol [18]. As the calculated activation energy is very close to this range of values, the nanoscale denitrification process seemed to show the characteristics of mass transport in addition to reaction control [68]. This result is different from those achieved with microscopic iron. Indeed, it was reported that the limiting step of the process with mZVI was the chemical reaction, rather than diffusion [67,68]. This is a profitable aspect of the use of nanoparticles, as the process that is controlled by the mass transport requires less activation energy [67].

2.2.6. Effect of Dissolved Ions

Similar to what is reported for mZVI, the nZVI performance can also be affected by the presence of other compounds in the solution. In particular, the impact of chloride was examined by using solutions of NaCl with concentrations of 0.05–0.5 M [89]. Contrary to what is reported for microscopic iron, the removal of nitrate by nZVI was reduced at high levels of Cl⁻ in the solution [89]. This result was ascribed to both the preferential accumulation of Cl⁻ on the iron surface and to the high production of OH⁻ due to the enhanced corrosion of Fe⁰, which precipitated as iron (hydr)oxides [89]. In other cases, the addition of different compounds to the solution produced increased removal rates during denitrification by nZVI. Khalil et al. used CuCl₂ in order to exploit the electrochemical and catalytic effects of copper ions [88]. The nitrate removal kinetics were around 3.5 times more than that by pristine nZVI, and the contact time was reduced by more than 67% [88]. However, in this application, high amounts of copper and ferrous ions remained in the solution [88].

The presence of other contaminants can also enhance the nitrate removal [87]. Indeed, when denitrification by means of nZVI was carried out in the presence of Cd^{2+} , increased removals with increasing cadmium concentrations were detected [87]. In particular, a complete denitrification was observed at 30 and 40 mg/L of Cd^{2+} [87]. This result was ascribed to the improvement in the electron flow that was facilitated by Cd^{0} and CdO, the presence of which was confirmed by the X-ray diffraction (XRD) analysis [87].

Thus, on the basis of the analysed works, the presence of other substances in the solution can produce different effects on the process performances. Indeed, the influence of dissolved ions is probably related to those of other operating parameters.

2.2.7. Supported nZVI

One of the most significant drawbacks of iron nanoparticles is the tendency towards agglomeration, which leads to a decrease in the specific surface area and, thus, to a reduction in the reactivity. To overcome this disadvantage, several support materials for nZVI have been used over time, such as magnesium oxide [95,96], biochar [97–99], activated carbon [100–102], chitosan fibres [103], hydrochar [104], plastics-derived carbon [105], zeolite [106,107], montmorillonite [108–110], bentonite [111–113], expanded graphite [114], graphene, and graphene oxide [115–119]. These supported nZVIs were used for the treatment of numerous contaminants, such as heavy metals, inorganic pollutants, and organic compounds. Some of them were also applied to enhance the nZVI reactivity and to increase the N₂ production during denitrification, as will be introduced in the following subsections.

Carbonaceous Materials

Some authors have tested carbonaceous materials as supports for nZVI [22–24,120–124]. Among carbonaceous materials, activated carbon is one of the most exploited because of its high surface area, its high sorption capacity, its reusability, and its availability from renewable sources [125]. Kamarehie et al. prepared granular activated carbon from grape wood, which was coated with nanoparticles of zero-valent iron and used for nitrate removal [120]. The authors report an efficiency higher than 99%. Moreover, increased removal rates with decreasing pHs were observed. The highest removal yield was achieved for pH values lower than its pH of zero charge (equal to 4.6). An increase in the initial nitrate concentration produced lower removal efficiencies, whereas the amount of nitrate removed per mass unit of adsorbent increased with the increasing nitrate concentration. On the other hand, the increase in the adsorbent concentration had a positive effect on the removal yields. The adsorption process was well simulated by the Langmuir model, while the kinetic was of the second order [120].

In another work, activated carbon (AC)-supported nZVI was optimized in order to reduce the iron oxidation and the poor pore diffusion of the AC [22]. The AC structure was modified by thermal nitric acid and by nitric acid-thermal treatments. The highest removal yields were obtained with the thermal treatment at 950 °C for 2 h. The authors also tested the impact of various interfering substances on the process. In particular, phosphorus reduced the nitrate removal efficiency by 22% [22]. Contrary to the other compounds, the presence of copper in the solution improved the nitrate removal [22]. This result is in accordance with the findings of other authors for unsupported iron [88].

Teng et al. tested denitrification through nZVI encapsulated in mesoporous carbon [121]. The material was prepared via a postsynthetic modification, which included carbon surface oxidation, the in situ ammonia prehydrolysis of an iron precursor, and hydrogen reduction [121]. The synthesized material was characterised by a surface area of 660–830 g²/m and by iron particles of 3–9 nm. The maximum removal capacity was obtained as 315 mg N/g Fe, and the nitrogen selectivity was up to 74%.

Wei et al. synthesised zero-valent iron/biochar composites (nZVI/BC) for denitrification [24]. The nZVI/BC was prepared by reducing the FeSO₄·7H₂O by means of NaBH₄ in the presence of biochar. A strong influence of the mass ratios of nZVI to biochar on the process was observed. The best efficiency was achieved at a mass ratio of 1:2. On the other hand, the variation in the pH did not bring about considerable changes in the removal yields, which were in the range of 75.0–97.0% for pHs of 2–12. However, increasing the nitrate concentration led to a decrease in the nitrate removal amount of the nZVI/BC that was due to corrosion and clogging. The process was found to follow a first-order kinetic. Finally, 60.2% of the nitrate that was reduced by nZVI/BC was converted to N₂.

Salam et al. experimented with the removal of nitrate by means of zero-valent iron nanoparticles that were supported on high-surface-area nanographenes (NGs) [23]. The nanocomposite was prepared by mixing iron nanoparticles with an appropriate quantity of NGs by using a mortar and grinding the mixture for 30 min to ensure homogeneity. The authors report a high removal of nitrate with a mass ratio between the nZVI and NG of 5:25. Furthermore, supporting the nZVI on the NG surface enhanced the removal process by 125.1%, compared to nZVI alone. The maximum removal yield (89.4%) was achieved at a pH of 2, which indicates an acid-driven process. The effect of the contact time was also studied, considering 30 mg of material, 10 mL of 50 mg/L of NaNO₃ solution, a temperature of 298 K, and a pH of 7. The equilibrium was reached within 16 hours of treatment, with an efficiency of 67.9% [23].

In a study, Fe, Ni, and Co nanoparticles that were coated with graphene oxide (GO) were used to remove nitrate from water [122]. The GO was prepared via the Hummer's method. The metal nanoparticles were placed on the surface of the GO by the in situ reduction of their metal chlorides via NaBH₄ in the presence of GO. The efficiency of the nitrate removal was tested by using solutions with a concentration of 5 mg/L at a pH of

6.9. The iron–GO composite produced the maximum removal yield, which was equal to 99%; while, for the Ni and Co, the efficiencies were, respectively, 95 and 94%.

The use of exfoliated graphite as a support material for nZVI was also tested [123]. Similar to the previous cases, $FeSO_4 \cdot 7H_2O$ was dissolved in a mixture of water and ethanol; then, exfoliated graphite was added, and KBH₄ was exploited as a reducing agent. The supported nZVI, with a particle size of 50–100 nm, yielded a higher nitrate removal efficiency than that of unsupported iron. The increasing loading of Fe on graphite, up to 15%, led to increased removal efficiencies. A loading of 20% resulted in a decrease in the removal yield, which was probably due to the aggregation of the nanoparticles during their deposition on the surface layer of the graphite. Contrary to the findings of other authors, this supports nZVI-generated ammonia as a reaction product [123].

In contrast, Wang et al. developed nZVI that was encapsulated within tubular nitride carbon, and it showed a nitrate removal efficiency of 92%, and a N₂ selectivity of 97% [124]. The tubular iron structure was characterised by a length of about 400–450 nm, a diameter of around 70–100 nm, a wall thicknesses of about 20–25 nm, and a surface area of 1445 m²/g. The authors also report the constant performance of the material by changing the pH from 5 to 11.

Clays

Clay minerals are hydrous aluminosilicates that are derived from the colloid fractions of soil and water, which are generally composed of minerals such as metal oxides, carbonate, and quartz [126]. Several tests were also conducted by using various clays as support materials for nZVI [21,127–130].

Natural zeolites are inorganic cation exchangers, which are abundant in nature and which are characterised by a high ion-exchange capacity and selectivity [131].

Sepehri et al. used natural zeolite-supported zero-valent iron nanoparticles to accomplish denitrification [21]. The material was prepared by using the reduction of ferrous iron with borohydride, in which zeolite acted as a porous-based support material. Nitrate reduction efficiencies greater than 84% were obtained by using this material. The reaction product was detected as ammonium, which was then completely adsorbed by the zeolite–nZVI composite. The initial pH of the solution affected the process performance. In particular, higher final concentrations were measured by increasing the pH from 2 to 10. Moreover, it was observed that the increase in the sorbent dosage causes a noticeable increase in the removal efficiency. The reaction of the nitrate reduction was represented by a pseudo-second-order kinetic, and the adsorption process was simulated by the Langmuir model.

In another work, the NaY zeolite supported different metal nanoparticles: Fe, Cu, Mn, Cu/Fe, and Mn/Fe [127]. Prior to synthesis, the NaY zeolite was thermally treated at 120 °C for 12 h. The metallic materials were prepared by a two-step process that involved ion exchange and liquid-phase reduction through NaBH₄. Finally, Fe, Cu, and Mn were deposited as zero-valent metals on the frame structure of a NaY zeolite. As for the nanocomposite of the nZVI and NaY zeolite, a nitrate removal efficiency of 100% was observed after 6 h of treatment at uncontrolled pH. Furthermore, a selectivity of N₂ near to 80% was achieved [127].

Attapulgite has also been used to support nZVI [128]. In particular, thermally modified attapulgite-supported nanoscale zero-valent iron (TATP-NZVI) was created by a liquid-phase reduction method. With the application of this material, the denitrification process performance was affected by both the DO concentration and the water temperature. Increasing the temperatures and decreasing the DO improved the removal yield. Furthermore, an efficiency of about 83.8% was reached at a pH of 7. However, contrary to the findings of the previous work, the main end product was ammonium [128].

Zhang et al. prepared pillared clay (PILC) from bentonite by intercalation with poly(hydroxo Al (III)) cations, and they used it as a support for zero-valent iron nanoparticles [129]. The iron–clay composite (Figure 3) was prepared by mixing the PILC with a solution of FeSO₄·7H₂O before the addition of the NaBH₄ solution. The material was found to be capable of completely removing the nitrate in 120 min. Furthermore, the authors state that the removal process was the result of a synergistic effect between the PILC and nZVI. In particular, the adsorption of a certain amount of nitrate on the pillared clay caused the increase in the concentration of nitrate in the vicinity of the iron surface, which facilitated the mass transfer of nitrate from the solution to the iron surface. Therefore, the reduction rate was accelerated [129].



Figure 3. TEM images of NZVI/PILC composite. This figure was published in: Zhang, Y.; Li, Y.; Li, J.; Hu, L.; Zheng, X. Enhanced removal of nitrate by a novel composite: Nanoscale zero valent iron supported on pillared clay. *Chem. Eng. J.* **2011**, *171*, 526–531. Copyright Elsevier [129].

Other authors tested, for denitrification, a commercial clinoptilolite zeolite as a support for nZVI, which was partially coated with zero-valent copper [130]. To prepare the material, firstly, the raw zeolite was crushed and sieved to obtain a mesh size in the range of 100–150. The zeolite was then washed with deionized water, was filtered, and was dried at 90 °C for 5 h. Afterwards, it was ion-exchanged with FeCl₂ aqueous solutions. The Fe²⁺ was reduced to Fe⁰ by means of NaBH₄. To coat the composite with Cu⁰, it was put in contact with a solution of CuCl₂. The dependence of the nitrate removal rate on the Cu²⁺ concentration was observed: the maximum efficiency was detected when the concentration was decreased to 5%. Although the material proved able to denitrify, a slightly high production of nitrite was observed [130].

Resins

Various types of resins have also been used to support nZVI [131–134]. Jiang et al. developed polystyrene resins that were functionalized with -CH₂Cl and -CH₂N⁺(CH₃)₃, and they obtained two hybrid nZVIs, which were denoted as Cl-S-ZVI and N-S-ZVI, respectively [132]. The materials were exploited for nitrate removal. For both the hybrids, the efficiencies showed a dependence on the pH and acidic conditions that enhanced the denitrification process. However, higher ammonia and lower nitrite productions were observed more for N–S–ZVI than for Cl–S–ZVI. Furthermore, 88.8% of the nZVI of the N–S–ZVI participated in the nitrate reduction, while the percentage of participating nZVI was 14.6% for the Cl–S–ZVI. Therefore, the N–S–ZVI resulted in a more efficient reductant than the Cl–S–ZVI. The authors ascribed this result to the different sizes of the nZVI particles of both hybrids.

In a study, the polymeric resin, D201, was used to support nZVI, and the effects of various iron distributions on the removal of nitrate were tested [133]. The D201–nZVI composite was prepared by adding a certain amount of the dry resin to a FeCl_4^- solution, and thus, the anionic FeCl_4^- was ion-exchanged with the counter Cl^- ions of D201. Once the composite was formed, the nZVI was obtained by a reduction in the FeCl_4^- via NaBH4. The distribution of the nZVI in the supporting material was controlled by adjusting the NaBH4 concentration. As the concentration of NaBH4 increased from 0.9 to 7.2%, the authors observed almost equal iron loadings, but the nZVI distribution changed from

the peripheral ring-like region to the whole matrix of the supporting polymer [133]. This resulted in higher ammonium production, a faster reaction rate, and more gaseous products during the reduction of nitrate and nitrite [133].

In another work, the same authors tested nZVI that was supported on the polymeric resin, D201, for denitrification under the influence of humic acid (HA) [134]. Indeed, HA can influence the electrostatic attraction of the nitrate and the quaternary ammonium group of the resins, and, at the same time, the reduction in the nitrate by nanoscopic iron [134]. A dependence of the nitrate reduction on the concentration of humic acid was evident. Indeed, for HA concentrations lower than 5 mg/L, the nitrate reduction; for higher concentrations, the competitive adsorption of tHA and nitrate was dominant, and the removal rate of the nitrate and the ammonia production decreased. However, for HA > 20 mg/L, an improved denitrification was reported. This result was ascribed to the reduction of Fe³⁺ to Fe²⁺ by the electron transfer of the HA [134].

In the presence of another contaminant (Pb²⁺), the nitrate removal by means of the nZVI that was immobilized on the polymeric exchange resin, DOW 3N, was investigated [135]. Similar to the previous case, the composite was obtained by adding 0.5 g of DOW 3N to a Fe³⁺ solution, which was then reduced to Fe⁰ by NaBH₄. The experiments were performed in the presence and absence of Pb²⁺. The denitrification efficiency in the absence of Pb²⁺ was 97%, which dropped to 87% in the presence of the other contaminant. This finding was attributed to the saturation of the available active sites by Pb²⁺. Although the removal yields were high enough in both cases, the final product was detected as ammonium [135].

Unconventional Supports

Zhou and Li synthesised polyethylene-packing-supported tea polyphenols–NZVI (TP–NZVI/PE) for denitrification [136]. In particular, tea polyphenols (TP) were used as the reducing agent, and polyethylene (PE) was used as the support material. To prepare the composite, at first, the surface of the PE packing was chemically modified in order to change the surface electro-negativity, which further improves the iron loading. The modified PE was added to a solution of FeSO₄; then, a TP solution was also added, and the final solution was stirred for 4 days at 50°C. The dry compound was used for nitrate removal. The efficiency that was obtained with the TP-NZVI/PE was about 25.5%, which was lower than that with bare nZVI (71.25%). Furthermore, the reaction product was ammonium. The low efficiency was explained by the high antioxidant activity of the tea polyphenols. However, when microorganisms were used in a combination of TP–NZVI/PE, the efficiency reached 79.88 \pm 0.17%, and the main end product was measured as N₂ (69.65%) [136].

Macroporous alginate was also utilized as a substrate for nZVI [137] (Table 2). Macroporous alginate-substrate-supported Fe⁰ nanoparticles were prepared by incorporating CO₂ inside an alginate solution, which was followed by freeze-drying and cross-linking with Fe^{2+} cations, which were, then, reduced with sodium borohydride. The Fe⁰ concentration in the composite had a minor effect on the process performance. Indeed, an increased amount of Fe⁰ only resulted in minor differences in the final removal efficiency. However, increasing the iron concentration accelerated the initial reaction rate by providing more reactive sites for the reduction of nitrate [136]. The authors report the enhanced nitrate reduction of the new composite compared to bare nZVI. However, the main reaction product was ammonium, while an amount of N₂ lower than 5% was detected [137].

Support Material	Efficiency *	Main Reaction Products	Refs.
Granular AC from grape wood	>99%	-	[120]
Commercial granular AC	>60%	NH_4^+ , N_2	[22]
Mesoporous carbon	315 mg N/g Fe	\dot{N}_2	[121]
Biochar	97%	N ₂	[24]
High-surface-area nanographene	>80%	NH_4^{+a} , N_2	[23]
Graphene oxide	99%	-	[122]
Exfoliated graphite	100%	NH_4^+	[123]
Tubular nitride carbon	92%	N_2	[124]
Natural zeolite	>90%	$\mathrm{NH}_4^{+\mathrm{b}}$	[21]
Nay zeolite	$\approx 100\%$	NH_4^{+b} , N ₂	[127]
Modified attapulgite	83.8%	\tilde{NH}_{4}^{+}	[128]
Pillared clay	100%	NH_4^+, N_2	[129]
Clinoptilolite partly coated with Cu ⁰	>60%	NH_{4}^{+c}	[130]
Microporous alginate	>96.5%	NH_4^+	[137]
Functionalized porous polystyrene resin	>80%	NH_4^+	[132]
Pyramid-structured silicon	100%	-	[138]
Polyethylene	≈25.5%	NH_4^+	[136]

Table 2. Nitrate removal efficiencies with nZVI supported on different materials.

* maximum value; adsorbed on the ^a nanographene; ^b zeolite; ^c clinoptilolite.

Anbia and Kamel used pyramid-structured silicon (PSi), made from metallurgicalgrade silicon powder, with wet alkaline etching to support nZVI [138]. The PSi/nZVI composite was tested for nitrate removal, and the process was only a little dependent on pHs in the range of 2–6.45. Indeed, an almost complete nitrate removal was achieved for each pH. Furthermore, compared to bare nZVI, the PSi/nZVI reached the equilibrium in a shorter amount of time. This result was ascribed to the good dispersion of the nZVI on the surface pyramid-structured silicon, which, thus, was accessible for nitrate [138].

3. Nitrate Removal by Other Zero-Valent Metals

3.1. Zero-Valent Aluminium

Although aluminium is traditionally used as a coagulant, it has recently gained attention thanks to its high reactivity [139]. Indeed, zero-valent aluminium (ZVA) holds a more negative redox potential ($E^0_{AI} = -1.662$ V) than zero-valent iron ($E^0_{Fe} = -0.44$ V) [25]. Therefore, ZVA has been used for the removal of various pollutants, such as heavy metals [140], organic compounds [141,142], dyes [143,144], and nitrate [25–29] (Table 3).

 Table 3. Nitrate removal efficiencies with different zero-valent metals.

Zero-Valent Metal	Dosage (g/L)	N-NO ₃ (mg/L)	Т (°С)	Oxygenated Conditions	pН	Efficiency *** (%)	Main Reaction Products	Refs.
Al ⁰	2.22	100 *	25	aerobic	10.25	75	NH ₃	[25]
	0.3	20	25	aerobic	10.7	62	NH ₃	[26]
	0.56	14	25	aerobic	13	100	NH ₃	[28]
Mg^0	2	50	20-24	aerobic	2	91	N_2 , NH_4^+	[30]
	6.67	20	20 ± 2	aerobic	3	100	N ₂	[17,31]
	0.387	200 *	25	aerobic	6	70.5	N_2	[32]
Cu ⁰	0.624 (CuO)	677	60	anaerobic	2.1-4.7 **	100	NH_4^+ , NO_2^-	[35]
	100	28	25 ± 1	aerobic	4.5	35	$\dot{NO_2^-}, N_2^-$	[36]
Zn^0	5	10 *	25	aerobic	1–2	93.2	$\bar{NO_2}$	[40]

* concentration expressed in terms of NO₃⁻; ** initial pH; *** maximum value.

Murphy studied nitrate removal by chemical denitrification through aluminium powder (350 mesh) in the presence of sulphate and chloride ions in water [25]. The tests were conducted at ambient temperature with 1 g of Al⁰ (in 450 mL sample), 100 mg/L of nitrate, sulphate, and chloride, and at pH values of 8, 10.25, and 11.5. The author reports a nitrate abatement of 75% at a pH of 10.25, and 50% at a pH of 11.5, while no reduction was observed at a pH of 8. This result was due to the protective oxide coating on the aluminium particles at a pH of 8, which was dissolved by increasing the pH [25]. Concurrently, the sulphate reduction took place during the denitrification test that was initiated at a pH of 11.5. At the end of 10 min of treatment time, almost the same reduction efficiencies were obtained for both the nitrate and sulphate. The main reaction product was ammonia (60–95%), but nitrite and nitrogen gas were also detected.

Comparable results were obtained by Luk and Au-Yeung, who used aluminium powder (200-325 mesh) to achieve denitrification [26]. The tests were conducted at 25 °C, with a molar ratio between the Al^0 and NO_3^- of 3.1, and with a pH ranging from 9 to 12. Similar to the findings of Murphy [25], the efficiencies were very low for pHs < 10.2. Furthermore, the abatements rapidly increased by increasing the pH from 10.2 to 11, and they decreased again for pHs > 11. Indeed, the authors report a stopping of the reaction at a pH = 12. In particular, the maximum efficiency (equal to 62%) was achieved at a pH of 10.7. Although the pH is a key factor for nitrate removal by means of aluminium powder, other parameters were also considered, such as the Al dosage, the temperature, the nitrate concentration, and the reaction time [26]. The optimal molar ratio between the aluminium and nitrate was individuated by varying this parameter between 2 and 13, which corresponds to a nitrate concentration of 10 mg/L, and to an aluminium concentration ranging from 40 to 250 mg/L. An increase in the nitrate removal efficiency was observed with increasing molar ratios up to a threshold value, after which the nitrate removal became asymptotic. As for the temperature, it was varied between 5 and 30 °C, and the optimum value for the process was found to be around 20–25 °C. The initial nitrate concentration ranged from 10 to 50 mg/L, and satisfactory removal yields up to 30 mg/L were obtained. After this point, the efficiencies dropped. The reaction was completed in 50 min of treatment, although almost half of the removal was achieved in the first 10 min. Finally, the authors also tested the treatment on real groundwater by using the optimum operating conditions, which are given by: T = 20.5 °C; $Al^0/NO_3^- = 7.8$; pH = 10.2; and a reaction time of 50 min. The tests were conducted on samples with nitrate concentrations of 8.2 and 21.6 mg/L, and mean removals of 62.1 and 58.1% were achieved, respectively [26].

In contrast to what is reported by Murphy [25] and Luk and Au-Yeung [26], Desai observed an optimum pH for chemical denitrification with aluminium powder (250–2000 μ m) that was equal to 12 [27]. Similarly, Esfahani and Datta achieved the maximum efficiency of the denitrification process through aluminium powder at a pH of 13 \pm 0.2 [28]. On the contrary, no abatements were observed at a pH of 10.8 \pm 0.2, even if various particle dimensions and molar ratios were considered. This result was ascribed to the formation of a thin adhering layer that is created on the surface of the particles by some reaction products, such as alumina (Al₂O₃), which can be eliminated by hydroxide promoters, such as NaOH [28]. Murphy reports that, at a pH of 8, the aluminium particles were covered by a protective oxide coating [25]. In some studies, this oxide layer that is present on the aluminium surface was removed through acid washing [29]. Indeed, no denitrification was observed by using raw ZVA, while, when acid washing was applied, the rate of nitrate removal increased to 1.219 h⁻¹. Furthermore, the addition of nickel and the use of ultrasound resulted in an increase in the process efficiency of both raw and acid-washed ZVA [29].

In some studies [25,26], the authors propose that the denitrification by zero-valent aluminium takes place in two stages. In the first stage, nitrate is reduced to nitrite by the following reaction:

$$3NO_3^- + 2Al^0 + 3H_2O \rightarrow 3NO_2^- + 2Al(OH)_3(s)$$
 (9)

In the second stage, the reaction proceeds from nitrite to either ammonia:

$$NO_2^- + 2Al^0 + 5H_2O \rightarrow NH_3 + 2Al(OH)_3 + OH^-$$
 (10)

or nitrogen gas:

$$2NO_{2}^{-} + 2Al^{0} + 4H_{2}O \rightarrow N_{2} + 2Al(OH)_{3} + 2OH^{-}$$
(11)

As seen in Equations (9)–(11), the formation of the Al(OH)₃ solid phase is considered during all stages. It is well known that its formation is strictly dependent on the solution pH. This dependency is not only owing to the hydroxide ion concentration, which determines the solubility of the Al(OH)₃, but is also because of the formation of soluble monomeric and polymeric aluminium hydroxo complexes. The concentrations of these hydroxo complexes are also determined by the pH. In alkaline conditions, $Al(OH)_4^-$ is the dominant species that determines the solubility of aluminium hydroxide. Its concentration increases with increasing pH, and it reaches up to high levels at alkali pH values. As a result of the formation of this complex species, the amount of $Al(OH)_3$ will decrease depending on the operation pH, as well as on the zero-valent aluminium dose that is applied. Therefore, for extremely high pH values, such as 12, $Al(OH)_3$ should be replaced with $Al(OH)_4^-$ in Equations (9)–(11).

On the basis of the analysed works, the denitrification process by the application of Al⁰ is strongly affected by the pH of the solution. Indeed, in most of the analysed works, unsatisfactorily abatements were achieved for pH values below about 10 [25,26,28]. This can be considered as the main drawback of the process. Indeed, increasing the pH to the high values that are reported in the cited articles would involve very high costs for the addition of the alkaline reagents. However, the process may be convenient when combined with other water treatments, such as softening, where the pH is normally raised to values above 9 [26].

Another crucial issue of the treatment with zero-valent aluminium is the dissolved aluminium content of the treated solution. As aforementioned, the aluminium concentration can reach up to a high level at the end of a denitrification application that is performed at extremely high pH values. Therefore, after the denitrification process, a post-treatment application, such as chemical precipitation, adsorption, or coagulation–flocculation, is required to minimize, or eliminate, the aluminium toxicity [140].

3.2. Zero-Valent Magnesium

Zero-valent magnesium (ZVM) is characterised by a higher reduction potential ($E^0_{Mg} = -2.363$ V) than ZVI and ZVA [30]. Furthermore, ZVM is less subject to passivation phenomena due to hydroxide precipitation, since Mg(OH)₂ (K_{sp} = 7.08 × 10⁻¹²) is more soluble than Fe(OH)₂ (K_{sp} = 7.943 × 10⁻¹⁶) [30,145]. However, this metal is much less applied in water remediation than zero-valent iron and aluminium. In the scientific literature, few works have been published on the removal of pollutants, such as hexavalent chromium [146–148], DTT [149], PCBs [150], and nitrate [17,30–34] (Table 3), by means of zero-valent magnesium.

Kumar and Chakraborty investigated chemical denitrification by magnesium powder (41.36 μ m) [30]. Several operating conditions were considered, such as the pH, the initial nitrate concentration, the Mg⁰ dose, and the temperature. The pH demonstrated that it is a crucial parameter. The authors report very low abatements when the solution pH was initially set at 2, 3, 4, and 6, without further corrections. This finding was attributed to the rapid increase in the pH to 10.8, which probably caused the passivation of the material by the precipitation of Mg(OH)₂. Indeed, the reactions between Mg⁰ and NO₃⁻ involve a consumption of protons [17,30,31]:

$$Mg^0 + NO_3^- + 2H^+ \rightarrow Mg^{2+} + NO_2^- + H_2O$$
 (12)

$$5Mg^0 + 2NO_3^- + 12H^+ \rightarrow 5Mg^{2+} + N_2 + 6H_2O$$
(13)

$$4Mg^0 + NO_3^- + 10H^+ \to 4Mg^{2+} + NH_4^+ + 3H_2O$$
(14)

This was confirmed by the experiments that were conducted at a fixed pH. Indeed, for a pH of 3 and below, the efficiencies were varied between 83 and 93%. On the other hand, the abatement decreased to 26 and 23% when the pH was kept at 5 and 7, respectively. The initial nitrate concentration also influenced the process efficiency. Nitrogen gas and ammonia were determined as the main end products. The authors also report a linear increase in the efficiencies with the increasing Mg⁰ dose. Increasing removal yields were observed with increasing temperatures from 10 to 50 °C. The process followed the first-order kinetic model with respect to the nitrate concentration. The process was found to be mass-transport-controlled on the basis of the activation energy (E_a), which is calculated as 17.7 kJ/mol [30].

In another study, the effects of some of the operating conditions on the denitrification process utilizing ZVM (60–510 μ m) were investigated [17]. The data indicate that the solution pH strongly influenced the nitrate removal performance. In particular, a pH of 3 resulted in the maximum removal yields, with an almost complete denitrification for initial concentrations of nitrate up to 60 mg/L and 2 g of Mg⁰. Under these conditions, the main reaction product was nitrogen gas. As is also reported by Kumar and Chakraborty [30], an increase in the solution pH to 5 and 7 led to a decrease in the process performances. The influence of the Mg⁰ dose on the process performance was also examined. The authors report increasing removal yields with increasing Mg⁰ doses up to a threshold value equal to 0.33 g of Mg⁰/mg NO₃⁻-N, after which no further improvements were observed. The process, in this case, was modelled by a pseudo-first-order reaction kinetics.

Similar results were observed when the denitrification was realized by Mg⁰ powder in a batch column system [31]. Moreover, in this case, the pH was demonstrated to be the most important parameter, since, under strongly acidic conditions (pH 3), efficiencies higher than 86.6% were obtained for each concentration $(10-140 \text{ mg NO}_3^-\text{-N/L})$ that was tested. The main end product was determined as N₂, and MgO was identified as a product of magnesium corrosion (Figure 4) [31]. Increases in the pH up to 5 and 7 caused a drastic decrease in the nitrate removal efficiency (<26%). The hydraulic recirculation velocity (HRV) (0.33–1.33 m/min) affected the process performance as well as the reaction end products. Although the nitrate removal efficiencies were improved with the increasing HRV, an HRV higher than 1 m/min created an instability problem in the packed bed. About 3% of the Mg⁰ was lost at an HRV of 1.33 m/min, which was due to fluidization. On the basis of this finding, 1 m/min was reported as an optimum HRV for a pH of 3, with an initial NO_3^- -N concentration of 20 mg/L, and a Mg⁰ dose of 2 g/L (in 300 mL nitrate solution). In contrast to the statement of Kumar and Chakraborty [30], an increase in the temperature from 20 to 30 and 40 °C had a negative effect on the process performance. This behaviour was attributed to the decrease in the superficial adsorption of the nitrate on the Mg^0 , which should be the limiting step of the process [31]. The process was well fitted by a pseudo-first-order model.

In contrast to the findings that were obtained from the aforementioned studies, Ramavandi et al. obtained a nitrate abatement of 70.5% for denitrification with Mg⁰ (<0.1 mm) at an initial pH of 6, and with a nitrate concentration of 200 mg/L (molar ratio between Mg⁰ and NO₃⁻ of 5) [32]. This difference could be explained by the operating conditions that were applied in the experimental studies, such as the Mg⁰ dose, the stirring mode and speed, and the volume of the solution to be treated. For instance, Ramavandi et al. performed their tests in 75 mL serum bottles that were placed in a rotary shaker [32]. The other researchers carried out their experiments on larger sample volumes of 2 L [30] and 300 mL [17] by using either a magnetic or a mechanical stirrer [17,30,32]. These different operating conditions may have promoted the contact between the solution and the reactive material, which produced satisfactory efficiencies at unfavourable pH values. At a fixed ratio of Mg⁰ and NO₃⁻ (5 in molar basis), the highest nitrate removal efficiency was obtained at the highest initial nitrate concentration (200 mg/L) [32]. Increasing removal rates with increasing temperatures from 5 to 60 °C were observed, and the first-order kinetic constants exhibited a temperature dependency that was consistent with the Arrhenius equation [32]. The activation energy was calculated as 20.39 kJ/mol, which reveals that the process was controlled by mass transport [32]. The authors also enhanced the process efficiency by coating copper onto the magnesium particle in order to produce bimetallic Cu/Mg particles [32]. This bimetal resulted in higher nitrate removal rates and the lower production of the undesired products (ammonia and nitrite) than those of Mg⁰ alone [32]. Denitrification by both the Mg⁰ and Cu/Mg particles proceeded through ammonia and nitrite as intermediates, with N₂ as the end product.



Figure 4. SEM image (**a**) and XRD (**b**) of fresh Mg⁰, SEM image (**c**) and XRD (**d**) of exhausted Mg⁰. This figure was published in: Siciliano, A.; Curcio, G.M.; Limonti, C. Chemical denitrification with Mg⁰ particles in column systems. *Sustainability* **2020**, *12*, 2984 [31].

Some hybrid systems were also developed to improve the efficiency of Mg⁰ during denitrification [33,34]. Mirabi et al. tested a hybrid system that was composed of ZVM powder and activated carbon (100–325 mesh) to remove nitrate from aqueous solution [33]. In their study, the pH was found to be the most impacting parameter. Indeed, a complete removal was achieved in about 20 min when the pH was kept constant at 3, while the efficiencies decreased when the pH was set to 7. However, a 62% removal yield was attained at an initial pH of 3, without further corrections. The Mg⁰ dose and the ratio between the magnesium and the activated carbon affected the process performance. At controlled pH, increasing removal rates were observed with increasing Mg⁰ amounts. However, when the pH was not controlled, the efficiency increased with increasing Mg⁰ powder dosages from 0.25 to 0.65 g/L, but no further improvement was obtained with an increase to 1 g/L. Similarly, the effect of the mass ratio was only observed when the pH was kept constant. Under pH-controlled conditions, an increase in the molar ratio led to increasing efficiencies. This result was ascribed to the facilitation of the electron transfer during the redox reactions that were performed by the activated carbon powder. The activated carbon provided more surface for the nitrate reduction [33].

Ileri et al. tested the use of ultrasound (US) to achieve denitrification by means of ZVM powder (50–320 μ m) without pH control [34]. In particular, Mg⁰ doses of 1.25–10 g/L, and ultrasound powers between 30 and 120 W, were experimented with. The authors observed an increasing rate of nitrate removal by US and Mg⁰ with increasing ultrasonic power and magnesium doses. The enhanced efficiency of the process, which is due to ultrasonic power, was considered to be the result of two mechanisms: the mechanical forces of acoustic waves directly removed the oxide films around the ZVM particles, and the pits and the cracks created on the particle surfaces increased the Brunauer–Emmett–Teller (BET) surface area [34]. The main byproducts were identified as nitrite and nitrogen gas, but N₂ became prevalent at elevated ultrasonic powers and magnesium doses.

Contrary to what is reported for Al^0 , the denitrification by means of magnesium is enhanced at low pH values. Indeed, except for one of the works mentioned, all the other authors report maximum efficiencies at acid pHs. Therefore, as for Al^0 , the continued use of reagents, in this case, to maintain acidic conditions, would entail a certain cost. However, similar to what was observed for nZVI, the process was found to have the characteristics of a reaction that is controlled by mass transport, which is an advantage, as it requires less activation energy. Moreover, contrary to the process that involves the use of zero-valent aluminium, the reaction between Mg⁰ and nitrate produces Mg²⁺ ions (Equations (12)–(14)). This product is naturally present in natural waters, and it does not pose a risk to ecosystems or humans [31,145].

3.3. Zero-Valent Copper

Zero-valent copper (ZVC) has also been used for the removal of various contaminants, such as hexavalent chromium [151], different toxic chlorinated organic compounds [152–154], dyes [155,156], and antibiotics [157].

Some studies were carried out to evaluate the efficiency of zero-valent copper in nitrate removal [35–38] (Table 3). Belay et al. (2015) synthesised zero-valent copper via the reaction between CuO and NaBH₄ [35]:

$$Cu^{2+} + 2BH_4^- + 6H_2O \rightarrow Cu^0 + 7H_2 + 2B(OH)_3$$
 (15)

The produced Cu^0 was used to realize the denitrification [35].

In particular, the experiments were conducted by pouring the CuO into a reactor containing 250 mL of NO_3^- solution, and the mixture was stirred for 12 h [35]. Then, the solution was purged with argon gas and heated to 60 $^{\circ}$ C, and NaBH₄ was added [35]. The tests were conducted considering high nitrate concentrations (677 mg/L), and by varying some of the operating parameters, such as the initial pH, the CuO dose, and the NaBH₄ dose. Although the authors observed the high removal of NO_3^- , a concomitant increase in the undesired byproducts (NO₂⁻ and NH₄⁺) was also detected. Therefore, even if the presence of N_2 as a product was individuated, it was not the main end product. The production of high amounts of NO_2^- was attributed to a more active reduction of the nitrate compared to other zero-valent metals, and to a lower affinity of the NO_2^- to the copper surface [35]. However, by increasing the CuO loading, not only an increase in the obtained pseudo-first-order rate constants was observed, but also a decrease in the production of NO_2^- and NH_4^+ was detected. Furthermore, by increasing the NaBH₄ concentration and the reaction time, it was possible to achieve the NO_2^- removal. On the basis of the obtained results, the authors state that NO_2^- was an intermediate product of the NO_3^- reduction [35]. Therefore, the nitrate was reduced, at first, to nitrite, and then to ammonium and nitrogen gas [35]. Furthermore, the decreasing nitrite concentration with increasing NaBH₄ was ascribed to a rapid conversion of NO_2^- to NH_4^+ [35]. This finding indicates that sodium borohydride is the main reducing agent of nitrite in the system [35]. The initial pH of the solution also affected the reaction. Indeed, a complete removal was obtained for initial pH values of 2.1–4.7. When the initial pH was not adjusted (pH = 6.8), an efficiency of 80% was attained. This result was ascribed both to the need for protons in the reaction, and to the removal of the copper oxide layer from the Cu surface at an acidic pH. Furthermore, it was

found that acid accelerated the hydrolysis reaction of NaBH₄, which could improve the reduction of nitrate [35].

In another work, Cu was supported on iron and aluminium oxide spheres that were prepared by the hybrid spheres method [36]. Materials with different amount of Fe₂O₃, (equal to 10, 30 and 50 wt%) were synthesised, each of which contained 10 wt% of Cu. The prepared materials were used for nitrate removal at 25 °C, a pH of 4.5, and considering a nitrate concentration of 2 mmol/L [36]. The highest nitrate conversion (35%) was observed for the composite containing the lowest amount of iron. This was attributed to the higher specific surface area of the material. However, the sample with the highest concentration of iron resulted in 100% N₂ selectivity. This result was probably due to the conversion of the formed nitrite into nitrogen gas that was performed by the Fe⁰ [36].

Satisfactorily high nitrate removal yields (up to 91.1%) were obtained by other authors through photocatalytic processes by using zero-valent copper nanoparticles that were in situ photodeposited onto P25 titania [37]. In particular, the highest removal yield was achieved when the highest concentration of glycerol, which was used as model hole scavenger, was applied. Other operating parameters, such as the pH and the nitrate concentration, also affected the reaction. For concentrations up to 150 mg/L of nitrate, abatements of over 93% were achieved. As for the pH, it was demonstrated to affect both the adsorption capacity towards the substrates of the surface titanol groups on the photocatalyst (amphoteric), as well as the position of the flatband potential of the photocatalyst, which decreased by 59 mV per pH unit [37]. However, the process was found to develop under both acidic and alkaline conditions. Moreover, the authors propose a linear model to describe the process for low concentrations of nitrate and a constant pH [37].

Recently, Kamali et al. tested the green synthesis of three-dimensional hexagonal-like zero-valent Cu following a facile sono-chemical route [38]. Cu^{2+} acetate [Cu(CH₃COO)₂] was exploited as a precursor, and a mixture of ethylene glycol (C₂H₄(OH)₂) and ethanol (1:1) was used as the solvent. The denitrification tests were carried out without pH control. The authors observed a removal yield of 85% during the first 30 min of treatment, which reached 90% after 2 h. However, in this case, the main reaction product was ammonia.

Although high efficiencies were achieved with zero-valent Cu, the release of this metal into the treated solution may be a cause for concern because of its toxicity. Indeed, damage in the kidneys, livers, and spleens of mice exposed to Cu^0 were observed [158]. Moreover, the phytotoxicity of copper nanoparticles was reported [158]. Furthermore, the reaction between NO_3^- and Cu^0 leads to the formation of Cu^{2+} , which can be toxic for aquatic organisms [159].

3.4. Zero-Valent Zinc

Our literature survey reveals that the usage of zero-valent zinc (ZVZ) as a nitratereducing agent is still under investigation. In effect, although some studies report the removal of different pollutants by ZVZ [160–162], only two papers on denitrification were individuated [39,40].

Carlson tested denitrification by means of granular zinc in a continuous flow column [39]. The author reports an efficiency of 99.6% when the initial nitrate concentration was 5 mM, and efficiencies of 99.1 and 98% for concentrations of 10 and 20 mM, respectively. In the study, the main end product of the reaction was determined as ammonia.

More recently, the effects of several operational parameters, such as the ZVZ dosage, the initial nitrate concentration, the temperature, and the pH, on the denitrification process were experimentally investigated [40] (Table 3). ZVZ powder was pretreated with hydrochloric acid (HCl) and was used at dosages of 2, 5, and 7.5 g/L [40]. The experiments were performed at varying reaction conditions: the initial NO₃⁻ concentration of 10–100 mg/L; a temperature of 25–60 °C; and a pH of 3–11. Furthermore, sulfate, bromate, and phosphate were also added to the nitrate solution in order to evaluate the effect of the coexisting anions on the process performance. The results show that increasing the ZVZ amount led to higher overall nitrate removal and also improved the nitrate reduction

efficiency per gram of ZVZ. However, when the zinc dosage was too high, the ZVZ particles tended to aggregate, which decreased the reactive surface of the ZVZ that was available for nitrate reduction. Therefore, the dosage of 5 g/L was considered the optimum for the process. When the nitrate concentration was increased, the material was still capable of removing considerable amounts of nitrate. However, for the initial concentration of 100 mg/L, the residual concentration was 70 mg/L after 120 min of treatment. Increasing the temperature enhanced the removal efficiencies, which was due to the facilitation of the mass transfer [40]. On the contrary, by decreasing the pH of the solution, the denitrification process was enhanced. The corresponding nitrate reduction efficiency was slightly lower when the coexisting anions were introduced into the nitrate solution. However, although the authors report effective nitrate removal, it should be noted that the main final nitrogen ion was nitrite, which is an undesirable product. For example, for the test conducted with 100 mg/L, the corresponding nitrite concentration was 19 mg/L [40]. In addition to the generation of unwanted nitrogen species, the toxicity of the zinc ion released from zinc metal could be a significant limitation of the process.

4. Final Considerations and Future Perspectives

In the present work, the chemical denitrification through various zero-valent metals was analysed. As reported above, among the zero-valent metals that are examined in this paper, iron is the most utilized.

In most of the studies that dealt with mZVI, it was concluded that acidic conditions enhanced the nitrate removal efficiency. As for the dissolved oxygen, different effects were observed. Indeed, some authors report a negative impact of the dissolved oxygen on the process. However, in other works, an improvement in the efficiencies was determined when the solution was exposed to air. Similarly, some conflicting conclusions were drawn for the effect of the initial nitrate concentration. Either positive or negative effects of the initial nitrate concentration on the process performances were ascertained, depending on their reaction conditions. The increase in temperature was reported to have a positive effect on the nitrate reduction. Furthermore, on the basis of the calculated activation energy, the process is controlled by the chemical reaction step.

During denitrification by means of nanoscopic iron, contrary to the case of mZVI, conflicting data on the influence of the pH were available in the scientific literature. Some authors state that the efficiencies improved when the process was conducted under acidic conditions, while others demonstrated that the reaction also proceeded under alkaline pH conditions. Moreover, different results on the impact of dissolved oxygen were described. Indeed, in some cases, aerobic conditions caused a decrease in the process performances. As for microscopic iron, this can be explained by the presence of an oxide shell that is created by corrosion compounds, which hinders the electron transfer from the core of the material to its surface. Other authors, instead, state that the strong ability of nZVI to donate electrons can lead to a consumption of dissolved O_2 at the beginning of the reaction, which, thus, can be considered anaerobic after the first instants. In terms of the initial nitrate concentration, similar findings to those reported with microscopic iron were published in the literature. However, the denitrification process through nZVI was defined as a masstransport-controlled reaction. This characteristic makes denitrification with nanoscopic iron more convenient in terms of energy consumption, since a process that is controlled by mass transport requires less activation energy than one in which the limiting step is chemical reduction.

In order to improve the applicability of nZVI, several authors used support materials. In effect, in some works, efficiencies higher than that achieved with unsupported iron are reported. Moreover, many researchers observed poor or no dependence of the process on the pH. Furthermore, it was often detected that the final reaction product was N₂, which is the most desirable product, as it volatilizes in the atmosphere and, thus, requires no further treatments.

N₂ was reported as the main end product of denitrification through ZVM. However, similar to mZVI, acidic conditions were required to achieve high nitrate removal efficiencies with Mg⁰. Nevertheless, this drawback was solved with the use of an ultrasound-assisted system. The temperature promoted the nitrate removal yield in most of the analysed studies.

The few works on the use of zero-valent copper and zero-valent zinc found a positive effect of low pH values on the nitrate removal. Despite this, satisfactory efficiencies of 80% were reported for zero-valent copper under uncontrolled pH conditions (an initial pH of 6.8). As for the ZVZ, the increase in the temperature enhanced the removal efficiencies. However, for both Cu^0 and Zn^0 , although satisfactory efficiencies were obtained, high productions of NO_2^- and NH_4^+ were observed.

Contrary to the other zero-valent metals, the denitrification process through zero-valent aluminium must be conducted at a pH > 10 in order to achieve a satisfactory performance. Some authors suggest that the treatment should be combined with other processes, such as water softening by using lime, in which the pH is increased to above 9. The process proved to effectively evolve at room temperature, and in the treatment of real contaminated water.

On the basis of the efficiencies that were obtained in the numerous analysed papers, and the simplicity of the treatment, the use of zero-valent metals for the removal of nitrate from water represents an attractive technique. However, some problematic aspects for the applicability of the various materials can be individuated. In particular, pH control during the treatment is a critical aspect. Denitrification by means of mZVI and ZVM requires stable acidic conditions to achieve satisfactory nitrate removal yields. The use of ZVA, instead, needs an alkaline pH. The use of chemicals to control the pH clearly negatively impacts on the costs of the treatment and could alter the quality of the water. Therefore, new systems should be developed to reach high efficiencies also under near neutral or uncontrolled pH conditions. For this purpose, the use of ultrasounds to remove oxide coatings on the surface of the metals could be thoroughly investigated. Moreover, the chemical modification of the materials may have positive effects on the reactivity without pH control. Another drawback to the applicability of some of the analysed metals is the transfer of ionic forms to the treated solution. Indeed, the reaction products of Fe⁰, and in particular, of Al^0 , Cu^0 , and Zn^0 , may be cause for concern because of the toxicity of the ions that are produced during the process. A post treatment to remove the unwanted dissolved ions could be necessary. To overcome this problem, the metals may be applied together with other materials that are able to adsorb the ions released in the solution. Regarding this aspect, the use of metals such as Mg⁰ is more advantageous, as its reaction products are not harmful and do not pose environmental risks.

The transformation of nitrate to ammonia and nitrite may represent another problematic feature of the use of some zero-valent metals. Also in this case, to avoid post treatment for the removal of nitrous and ammoniacal species, the use of more suitable metals should be promoted. In this regard, the Mg^0 , under the optimal operating conditions, ensures, mainly, the generation of nitrogen gas. In addition, the nanoscopic ZVI that is supported on proper materials leads to a high production of N₂. Moreover, some supporting materials, such as zeolite, could adsorb the residual ammonium, which would avoid its persistence in the treated water. On the basis of these considerations, it emerges that the development of support materials for various zero-valent metals would be an interesting future prospect of the research. Moreover, the synthesis of bimetallic composites may be a future direction in order to increase the effectiveness of the process and the selective generation of N₂. Furthermore, additional research is necessary to test the application of the process at an industrial scale and in field conditions.

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