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Removal of Nitrate from Drinking Water by Ion-Exchange Followed by nZVI-Based Reduction and Electrooxidation of the Ammonia Product to $N_{2(g)}$

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Abstract: Ion-exchange (IX) is common for separating NO_3^- from drinking water. From both cost and environmental perspectives, the IX regeneration brine must be recycled, via nitrate reduction to $N_{2(g)}$. Nano zero-valent iron (nZVI) reduces nitrate efficiently to ammonia, under brine conditions. However, to be sustainable, the formed ammonia should be oxidized. Accordingly, a new process was developed, comprising IX separation, nZVI-based nitrate removal from the IX regeneration brine, followed by indirect ammonia electro-oxidation. The aim was to convert nitrate to $N_{2(g)}$ while allowing repeated usage of the NaCl brine for multiple IX cycles. All process steps were experimentally examined and shown to be feasible: nitrate was efficiently separated using IX, which was subsequently regenerated with the treated/recovered NaCl brine. The nitrate released to the brine reacted with nZVI, generating ammonia and Fe(II). Fresh nZVI particles were reproduced from the resulting brine, which contained Fe(II), Na^+, Cl^- and ammonia. The ammonia in the nZVI production procedure filtrate was indirectly electro-oxidized to $N_{2(g)}$ at the inherent high Cl^- concentration, which prepared the brine for the next IX regeneration cycle. The dominant reaction between nZVI and NO_3^- was described best (Wilcoxon test) by $4Fe_{(s)} + 10H^+ + NO_3^- \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O$, and proceeded at >5 $mmol \cdot L^{-1} \cdot min^{-1}$ at room temperature and $3 < pH < 5$.

Keywords: nitrate reduction; nZVI; electrooxidation; drinking water; ion exchange

1. Introduction

Regulations restricting nitrate concentration in drinking water are in place in both the developed and developing world. The US environmental protection agency (US EPA) set a maximum contaminant concentration of 10 mg N/L (i.e., 45 mg/L as NO_3^-) for drinking water. Similarly, the maximum acceptable concentration of nitrate in potable water, recommended by the World Health Organization (WHO) is 50 mg/L as NO_3^- [1]. The Israeli Public Health Regulations threshold for nitrate concentration is 70 mg NO_3^-/L, and in case the water is treated to reduce the nitrate concentration, the allowed concentration drops to 50 mg NO_3^-/L.

No consensus exists on the most appropriate technology to remove nitrate from drinking water. The technologies applied at full scale may be divided into separation techniques, biological treatments, such as denitrification and assimilatory nitrate reduction, chemical reduction techniques and combinations thereof. Direct nitrate reduction in drinking water often necessitates a post treatment step in order to remove residual matter comprised of organic matter, microorganisms and turbidity-causing agents. This is especially problematic in the case of biological treatment. Although direct biological treatment applied on drinking water tends to induce psychological public rejection [2], such methods have been successfully implemented at full scale. Common NO_3^- separation techniques include

electro-dialysis, reverse osmosis and ion-exchange (IX). Anionic IX is a relatively selective separation technique and probably the most popular method for NO_3^- removal from drinking water. IX involves passage of nitrate-contaminated water through strong base anion (SBA) exchange resins, on which nitrate ions are adsorbed, typically in exchange for chlorides. Regeneration is usually conducted with a concentrated NaCl solution. The spent IX brine is typically comprised of several hundred mg/L of nitrate (as N) along with a very high NaCl background. Such a solution is problematic for disposal to the sewer or to receive water bodies, and normally requires further treatment prior to discharge. For IX to be an economic solution, the brine has to be treated for nitrate removal and recycled. A possible option for nitrate removal at high NaCl background conditions is metal-induced chemical reduction.

Several authors already suggested combining ion-exchange separation and nitrate reduction from the regeneration solution (preferably to $N_{2(g)}$) to enable the reuse of the latter, and thereby reduce the cost of the IX process and its environmental impact. Pintar et al. [3] and Kim et al. [4] combined an IX step with a Pd-Cu based catalytic nitrate reduction process. Shi et al. [5] mounted bimetallic Fe-Pd nanoparticles on a chelating resin (DOW 3N) and showed nitrate removal of >95% and increased selectivity to $N_{2(g)}$ as the nitrate reduction end product at increased Pd content and solution pH. Meng et al. [6] proposed a desorption–bioregeneration technique for reducing nitrate in diluted IX brines (9 to 31 mS/cm) to nitrogen gas. Dortsiou et al. [7] applied direct electrochemical reduction of nitrate on the brine of an ion-exchange operation and reported (as could be expected) low current efficiency that translated into high operational costs. Kabay et al. [8] used an electro-dialysis ion-exchange hybrid process for removal of nitrate from groundwater. Bergquist et al. [9] also combined ion-exchange with catalyst nitrate reduction.

Chemical nitrate reduction has been widely studied using mostly zero valent iron (ZVI), $Mg_{(s)}$ and $Al_{(s)}$ as the electron donors [10]. Upon the use of these metals as reducing agents, nitrate has been reported to be reduced to TAN (total ammonia nitrogen, i.e., the combined concentration of NH_4^+ and NH_3), to nitrite (NO_2^-), and also to nitrogen gas ($N_{2(g)}$), which is clearly the preferable product from the water quality point of view. Zero-valent magnesium is a highly reactive reducing agent; however, it is relatively costly and also becomes rapidly covered with a thin magnesium oxide layer upon contact with water, which eventually hinders its reactivity towards nitrate [11]. Drawbacks reported for aluminum as a reducing agent were low efficiency (40–50%), low effectiveness at initial nitrate concentrations higher than 30 mg N/L and potential water contamination with residual Al^{3+} concentration remaining in the water [12]. In general, the use of metals as reducing agents results in release of reduced metal ions (Fe^{2+}, Mg^{2+} and Al^{3+}, respectively), that sometimes require further treatment. More importantly, the product of nitrate reduction by metals is apparently (mostly) TAN, which also has to be removed from the water.

Considerable efforts have been dedicated in recent years to studying the chemical reduction of nitrate by nano zero valent iron (nZVI) due to its large specific surface area and high reactivity, as compared to other reducing agents [13]. In this respect, different stoichiometric reactions have been suggested for describing the nZVI enhanced NO_3^- reduction [13–15]. Apparently, only one study [16] concluded that nitrate was reduced predominantly to $N_{2(g)}$ as the end product. All other studies reported that between 85% and 90% of the nitrate was reduced to TAN and only the rest of the nitrate (i.e., less than 15%) was reduced to $N_{2(g)}$ (e.g., [17–19]). Other studies (e.g., [13,14]) reported that almost 100% of the NO_3^- was reduced to TAN. The reports on the portion of $N_{2(g)}$ vs. TAN formation have been thus far based mainly on nitrogen species mass balance calculations [16,17]. Accordingly, the following reaction is considered by many (e.g., [17,20]) to represent the predominant reaction between nZVI and NO_3^- at the acidic to neutral pH range:

$$4Fe_{(s)} + 10H^+ + NO_3^- \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O. \tag{1}$$

However, several studies reported that, on top of ammonium formation (the main end product), nitrite is also produced, although at much lower concentrations [14,21].

The fact that nitrate reduction by nZVI leads predominantly to the formation of TAN (or to nitrite) significantly detracts from the attractiveness of the approach for drinking water treatment [22], and it is clear that, in order for the process to be feasible, it needs to be coupled with an efficient (and relatively cheap) physical-chemical TAN removal strategy.

Kinetics wise, several parameters have been reported to affect the reaction rate between nitrate and nZVI. These include the pH value, presence of nZVI mass beyond the stoichiometric requirement, the initial nitrate concentration and the chloride ion concentration. Contradicting reports exist regarding the effect of pH on the reaction rate. Comparing results from different works is problematic since, in some studies, the pH was not controlled and thus fluctuated in a wide range covering basic and acidic values [15,19,23], while, in others, it was maintained at a relatively wide, but acidic range of pH 2–5 [17,24]. Several works (e.g., [19,20,24,25]) reported that nitrate reduction by nZVI proceeded more rapidly at acidic conditions. This observation seems reasonable, since protons are consumed in Equation (1). Siciliano [24] also suggested that the higher reaction rate at low pH might be related in part to H^+-induced iron oxidation occurring at the acidic solutions. Accordingly, these authors defined the mechanism as "acid-driven surface mediated process".
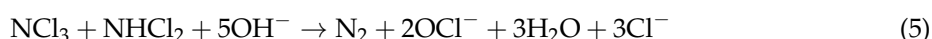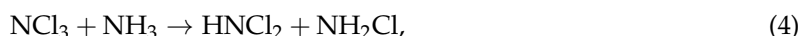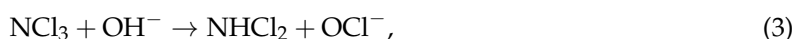
Another parameter that varies in reported studies is the initial molar concentration of the reactants, i.e., nitrate and nZVI, and the initial molar ratio between them. The stoichiometric ratio between Fe and NO_3^- according to Equation (1) is 4. However, in most experimental works, Fe was applied in large excess. For example, Yang and Lee [17] tested two Fe to NO_3^- molar ratios: 14.72 and 7.36, while maintaining the same initial nitrate concentration. They reported on increased reaction rate at the higher Fe to NO_3^- ratio. A similar observation was reported by Siciliano [24]. On the other hand, Yang and Lee [17] reported that the nitrate reduction rate decreased at a higher Fe to NO_3^- ratio when lower nitrate concentrations were applied, while the Fe dosage was maintained constant (at pH 4). This apparent contradiction can be a consequence of the effect of the reactant concentrations. That is, the concentration of NO_3^- and Fe themselves have an effect on the rate and not only the ratio between them. This is also shown by another comparison, in which a higher reaction rate was reported at the same Fe to NO_3^- molar ratio when the initial Fe and NO_3^- concentrations were higher [17]. However, examining the results reported by Siciliano [24] leads to opposite conclusions: lower reaction rates were observed when the reactant concentrations were elevated, while the molar ratio between Fe and NO_3^- was kept almost constant. In addition, a decrease in the reaction rate at higher nitrate concentrations (accompanied by a decrease in the molar Fe to NO_3^- ratio) was observed in experiments in which the pH was both controlled and not controlled ([24] and [15], respectively). When the pH was not controlled, high nitrate concentrations promoted faster reaction and thus a rapid pH increase (due to proton consumption), at which conditions of the reaction kinetics slowed down, as mentioned above. To sum up, both the initial reactant concentrations and the Fe to nitrate ratio seem to affect the reaction rate, and, at different conditions, the rate limiting factors are apparently different.

Contradicting results have also been reported on the effect of the chloride ion concentration on the kinetics of the nZVI-NO_3^- reaction: Choe et al. [26] concluded that a high chloride concentration enhanced Fe^0 oxidation by H^+, thereby enhancing the reactivity of Fe^0 for NO_3^- reduction. On the other hand, Hwang et al. [23] claimed that NaCl adsorption on the surface of the nZVI inhibited the rate of iron oxidation. Similarly, Xiong et al. [18] claimed that the presence of 6% NaCl (w/w) decreased the observed reaction rate constant (K_{obs}) by 30% compared to the rate in fresh water (0.30 min^{-1} compared to 0.21 min^{-1}), due to "double-layer compression effects", which led to increased agglomeration of the nZVI particles.

To sum up the kinetics part: the results of most of the works reviewed by us show that the time required for complete nitrate removal from an initial nitrate concentrations lower than 120 mg N/L was typically 30 min or more [13,16,19,24]. On the other hand, working with a very high initial nitrate concentration of 10,000 mg N/L, Ryu et al. [14] reported a very rapid removal rate (reduction of 5000 mg N/L in one minute). It seems, however, that the reaction rate of nitrate reduction by nZVI has not been tested thus far at the conditions relevant to the current work, i.e., NO_3^-

concentration expected in IX regeneration brines (~250 mg/L) and in the presence of a very high Cl^- background (1–2 M). Excluding Ryu et al. [14], the reaction between nZVI and nitrate has been thus far investigated with relatively low nitrate concentrations, i.e., <120 mg N/L, and also at relatively low Cl^- concentration background (e.g., [13,15,16,23,26]), since these are the conditions typical to nitrate-polluted drinking water.

The current work examines the application of nZVI-enhanced-nitrate-reduction for reusing the regeneration solution that forms in nitrate separation ion-exchange applications. In order to fully recycle the regeneration solution, the end product should be $N_{2(g)}$, rather than TAN. To this end, an additional step should be applied to oxidize TAN to $N_{2(g)}$. The indirect ammonia electrochemical oxidation approach has been proven highly effective in solutions characterized by high Cl^- concentration, for example, for the removal of TAN from IX regeneration solutions treating recirculated aquaculture system water and swine wastewater [27,28]. From the mechanism standpoint, Gendel and Lahav [27] showed that under the conditions prevailing in electrochemical reactors treating a TAN-containing solution characterized by low buffering-capacity and very high Cl^- concentration, the Cl_2 generated on the anode reacts with NH_4^+ to form trichloramine (Equation (2)), which further reacts extensively in the bulk electrolyte solution to produce nitrogen gas (Equations (3)–(5)):

$$3Cl_2 + NH_4^+ \rightarrow NCl_3 + 3Cl^- + 4H^+, \tag{2}$$

$$NCl_3 + OH^- \rightarrow NHCl_2 + OCl^-, \tag{3}$$

$$NCl_3 + NH_3 \rightarrow HNCl_2 + NH_2Cl, \tag{4}$$

$$NCl_3 + NHCl_2 + 5OH^- \rightarrow N_2 + 2OCl^- + 3H_2O + 3Cl^- \tag{5}$$

The current efficiency recorded for TAN removal in batch electrolysis experiments was as high as ~92% [27].

The current work focuses on two topics: (a) the development of a complete process which combines IX separation and nZVI-based nitrate reduction, followed by indirect ammonia electro-oxidation; (b) determining the nZVI-based nitrate reduction reaction and its kinetics in the unique conditions prevailing in the suggested process. The investigation of the reaction included quantitative determination of end products as a function of pH and time; the effect of high Cl^- concentration on the reduction kinetics; the ability to re-synthesize nZVI from Fe(II) present in the brine as a result of the NO_3^- reduction, that is, at high background Cl^- concentration and relatively low Fe(II) and TAN concentrations.

Description of the Proposed Process

A schematic layout of the combined process appears in Figure 1. The process comprises an integration of an ion-exchange stage with chemical reduction by nZVI and electrochemical treatment stage. The process goal is to treat drinking water containing nitrate and recycle the IX regeneration solution. The first and second steps (Figure 1) are the ion-exchange adsorption and regeneration steps, respectively. Regeneration was conducted with 8% NaCl solution. The third step (nitrate chemical reduction by nZVI) was applied on the brine leaving the IX regeneration process. This brine contains a high NaCl concentration along with a considerable concentration of NO_3^- (several hundred mg N/L). At the end of the third step, the brine contains (mainly) dissolved Fe(II), ammonium and practically no nitrate, along with high chloride and sodium ion concentrations. This brine flows to the fourth step in which nZVI particles are reproduced from dissolved Fe(II) in order to be used in the subsequent third step. In the fifth and final step, electrochemical oxidation of NH_4^+ to $N_{2(g)}$, is applied on the filtrate of the fourth step, which contains TAN and a high Cl^- background. This allows for recirculation of the regeneration solution.
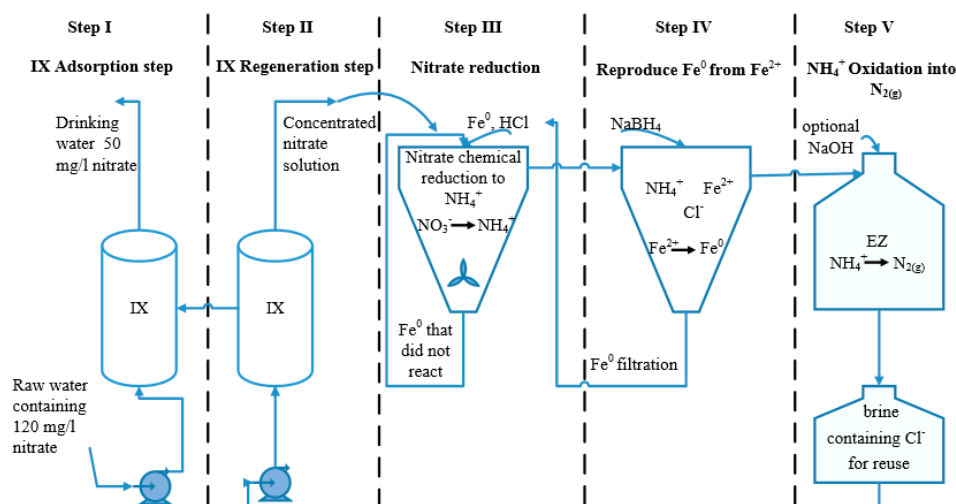
Figure 1. Schematic of the suggested process.

2. Materials and Methods

2.1. Materials

Synthetic drinking water was prepared with characteristics typical to contaminated wells in Israel, i.e., nitrate, sulfate, chloride and alkalinity concentrations of 27 mg N/L, 19 mg S/L, 265 mg/L and 120 mg/L as $CaCO_3$, respectively, by dissolving analytical sodium-based salts in distilled water.

Ion-exchange resins: Purolite A520E and Purolite A300 were examined. Purolite A520E is a macroporous strong base resin, often applied for removal of nitrate from drinking water. Purolite A300 is a strong base resin with high operating capacity and good regeneration efficiency. Both resins were obtained free of charge from Purolite Int. Ltd. (Barcelona, Spain).

2.2. Ion-Exchange Experiments

NO_3^- adsorption and desorption experiments were carried out using two 34 mm internal diameter PVC columns, each filled with 635.5 mL of resin. A peristaltic pump was used to attain constant flow rates of 23.6 bed-volumes per hour (BV/h) into each column during the adsorption step, and 4.25 BV/h during the regeneration step. In addition, 8% (i.e., 1.37 M) NaCl solution was used for regeneration. Adsorption and regeneration steps were carried out alternately for three consecutive cycles on each column.

2.3. Synthesis of Nano Zero Valent Iron (nZVI)

The entire procedure (preparation of nZVI and subsequent reaction with nitrate) was carried out inside an anaerobic compartment to prevent reaction with atmospheric oxygen.

2.3.1. Synthesis of nZVI via Fe^{3+} Reduction

The nZVI synthesis method was as described in Wang and Zhang [29]. In brief, 3.0 M $NaBH_4$ aqueous solution was added dropwise to a 1.0 M $FeCl_3$ aqueous solution at ambient temperature and fully stirred anaerobic conditions. Fe^{3+} was reduced to form nZVI by the following reaction:

$$Fe(H_2O)_6^{3+} + 3BH_4^- + 3H_2O \rightarrow Fe^0(s) + 3B(OH)_3 + 10.5H_2. \tag{6}$$
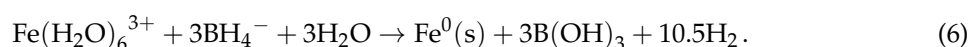
The solid cake was filtered and washed with acetone and distilled water. The wet solid cake was weighed and immediately used in the nitrate reduction experiments.

2.3.2. Synthesis of nZVI via Fe^{2+} Reduction

Examination of Step IV (Figure 1) was conducted by modifying the nZVI synthesis method offered by [29], as follows: nZVI were synthesized by adding 550 mL 0.285 M $NaBH_4$ aqueous solution dropwise to 550 mL 0.09 M Fe^{2+} aqueous solution (prepared by dissolving $FeCl_2 \cdot 4H_2O$) at ambient temperature and stirred anaerobic conditions. The Fe(II) solution contained also 1.27 M NaCl and 0.012 M NH_4Cl as background. That is, the Fe(II) solution simulated the solution leaving the nitrate reduction step (Step III in Figure 1). Fe^{2+} was reduced according to the following reaction:

$$Fe(H_2O)_6{}^{2+} + 2BH_4{}^- \rightarrow Fe_{(s)} + 2B(OH)_3 + 7H_{2\,(g)}. \tag{7}$$
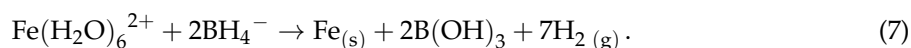
The washing and filtration procedures of the nZVI were identical to those mentioned in Section 2.3.1.

2.4. Nitrate Reduction by nZVI: Batch Experimental Procedure

nZVI-induced nitrate reduction was examined in the spent solution collected from the ion-exchange regeneration step. A weighed mass of fresh nZVI wet cake (corresponding to 2.5 g of nZVI on a dry basis) was dosed into each beaker containing 200 mL of spent IX regeneration solution to attain a ratio of ~12 between initial Fe and $NO_3{}^-$ (M/M). The beakers were constantly mixed using a magnetic stirrer. The pH was maintained at the chosen acidic range by manual dosage of concentrated HCl solution. HCl consumption was recorded. When the reaction had completed, the Fe particles that remained in the beaker were allowed to settle and the supernatant was filtered through 0.45 μm filter paper, and subjected to analysis. The whole procedure was conducted inside an anaerobic chamber under nitrogen gas atmosphere.

2.5. Electrolysis Experiments

A synthetic solution containing $NH_4{}^+$ and Cl^- (and naturally also Na^+) at concentrations similar to those attained at the end of the nZVI re-synthesis step (step IV in Figure 1), i.e., 220 mg N/L (lower than the initial concentration due to acid dilution) and ~45,000 mg/L, respectively, was prepared by dissolving NH_4Cl and NaCl in distilled water. Note that this step was applied following the re-synthesis of nZVI from the dissolved Fe(II), thus the dissolved Fe(II) concentration in the solution of the electrolysis step was negligible. pH and ORP were recorded throughout the experiment. Samples for TAN analysis in the effluent were collected every 7 minutes. The electrolysis cell (Klorogen M10, monopolar, parallel plate, TiTan, Chennai, India) was operated at 5 A. The pH of the regenerant solution was controlled at pH 7 during the electrolysis step by automatic NaOH (0.7 N) dosage.

2.6. Analyses

Chloride ion concentration was measured by the argenometric method, according to Standard Methods [30]. $SO_4{}^{2-}$ and dissolved Fe concentrations were analyzed by ICP-OES (Thermo Scientific, Schaumburg, IL, USA). TAN was determined by the modified salicylate method [31]. $NO_3{}^-$ and $NO_2{}^-$ concentrations were measured colorimetrically using an auto-analyzer (QuickChem 8500, Lachat Instruments, Milwaukee, WI, USA) according to Standard Methods [30]. Alkalinity was measured by the Gran titration technique. Fe(II) was analyzed using the modified phenanthroline method proposed by Herrera et al. [32].

2.7. Statistical Analysis

Differences between actual and calculated acid consumption were examined using the Wilcoxon test (using Matlab code). Forty independent couples of actual HCl dosage and calculated consumption

were compared. The purpose of this statistical test was to evaluate the validity of the assumption that Equations (1) and (8) are indeed the dominant reactions in the nZVI nitrate reduction step:

$$Fe_{(s)} + 2H^+ \rightarrow Fe^{2+} + H_{2(g)}.$$

(8)
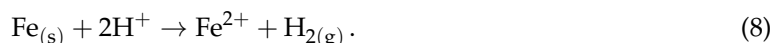
3. Results and Discussion

3.1. Nitrate Adsorption and Regeneration

Figure 2a,b shows average ($n = 3$) breakthrough curve results obtained by passing the simulative contaminated well water through the ion-exchange resins (A520E and A300) at 2.5 min hydraulic retention time. The target nitrate concentration in the treated water (50 mg NO_3^-/L) appears on the plots as a solid line. Comparing the results of the two resins revealed that, as expected, both adsorbed NO_3^- well. After 400 BV, the cumulative NO_3^- concentrations were 0.727 mM and 0.820 mM in the product solution of A520E and A300, respectively (the allowed nitrate concentration is 0.812 mM). Nevertheless, A300 adsorbed more sulfate and alkalinity then A520E. Therefore, from both the water quality and economic standpoints, A520E was found to be slightly advantageous. Figure 3a,b shows the average ($n = 3$) cumulative concentrations of relevant anions at the outlet of the regeneration steps of A520E and A300, respectively. Figure 3 shows that both resins were regenerated efficiently. As expected, due to the higher adsorption of sulfate and alkalinity by the A300 resin, its effluent consisted of higher concentrations of bicarbonate and sulfate. Based on mass balance calculations, it was concluded that 95% of the NO_3^- adsorbed in the adsorption step was released after 24 BVs from the A520E resin, as compared to 90% released from the A300. Similar conclusions are reported by Primo et al. [33] and Shams [34]. In conclusion, both resins are adequate for the suggested process; however, A520E's performance was slightly better. Accordingly, all further work reported in this paper was conducted on the brine resulting from the regeneration of A520E.
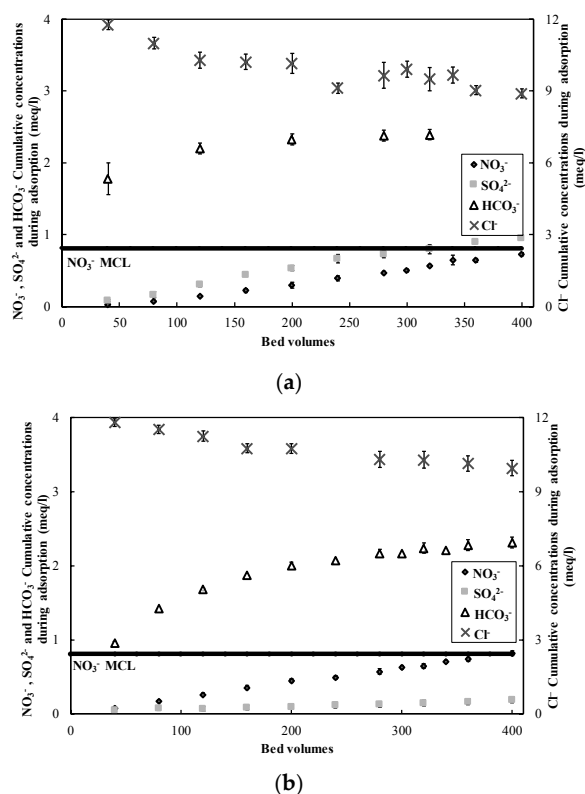

(a)

(b)

Figure 2. Results of ion exchange (IX) adsorption experiments: average ($n = 3$) cumulative concentrations during adsorption step using A520E (**a**) and A300 (**b**) resins (HRT = 2.5 min).
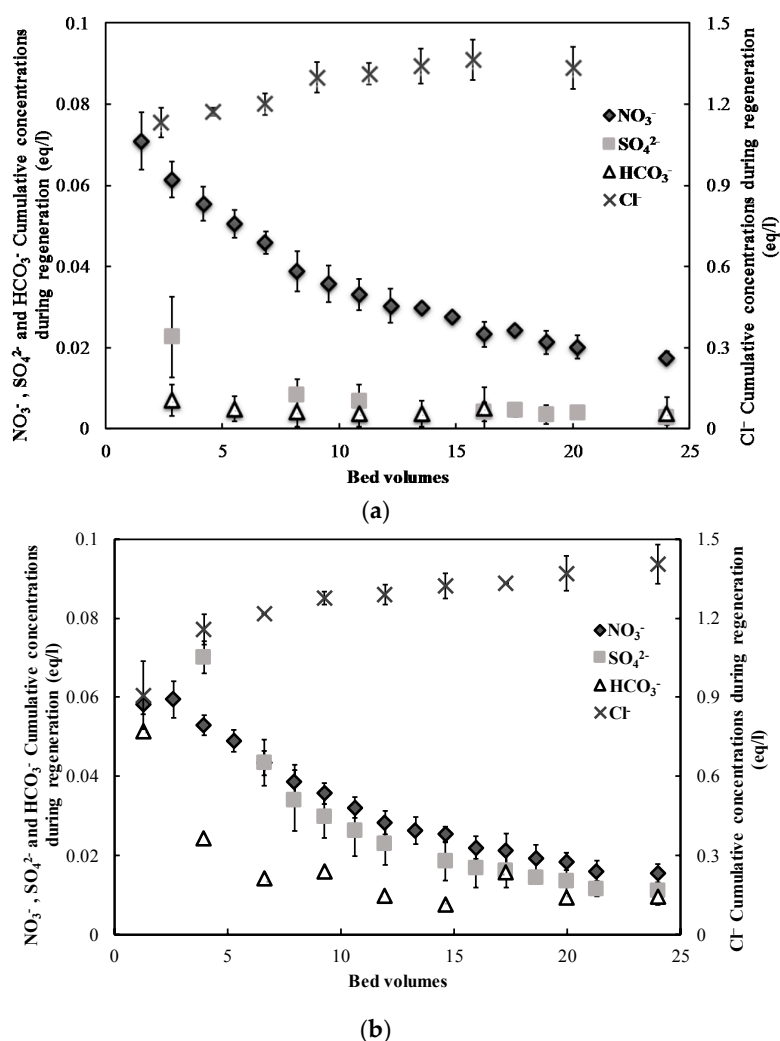
Figure 3. Results of IX regeneration experiments: average (*n* = 3) cumulative concentrations during regeneration step using A520E (**a**) and A300 (**b**) resins (HRT = 14 min).

3.2. nZVI-Induced Nitrate Reduction

3.2.1. Quantitative Determination of the Dominant Reactions

Reduction of nitrate using nZVI as the reducing agent was conducted by adding nZVI slurry to the solution attained from regenerating the A520E resin (see Table 1 for solution composition) at various conditions. The results obtained in all the experiments were roughly similar, as shown in Table 2.

Table 1. Characterization of the two solutions used in the NO_3^- reduction experiment: The cumulative A520E regeneration brine (after 24 BV); and a synthetic solution used in the nZVI reduction experiments for examining the effect of Cl^- absence (see Section 3.3).

| Solution	SO_4^{2-} (mg S/L)	NO_3^- (mg N/L)	Cl^- (mg/L)	Alkalinity (mg $CaCO_3$/L)
Regeneration solution	44	253	45,246	162
Synthetic solution	64	256	0	281

Table 2. Average operational conditions and results ($n \geq 4$) of nZVI-enhanced nitrate reduction experiments: ratio between mass of relevant components at the end of the experiment and the initial NO_3^- mass.

Exp. No.	pH Range	Duration	End Product Concentration Relative to $[NO_3^-]_{initial}$		Ratio between Acid Dosage and Nitrate Reduced	Mass Balance Error (Actual vs. Anticipated Acid Consumption)
		min	TAN (%)	Fe^{2+} (mol/mol)	meq/mg NO_3^- as N	%
#1	2–4	41	90.13	8.074 ± 0.715	1.28 ± 0.09	0.054
#2	3–5	52	91.76	7.277 ± 0.169	1.17 ± 0.02	−253
#3	4–6	38	87.89	6.968 ± 1.007	1.13 ± 0.11	0.939
#4	5–7	30	98.70	4.300 ± 0.291	0.68 ± 0.12	−12.153
#5	3–5	25	100.0	4.673 ± 0.114	0.82 ± 0.01	0.676
#6 *	3–5	28	100.0	4.264 ± 0.158	0.73 ± 0.01	−4.172
#7 **	3–5	28	100.0	5.540 ± 0.403	0.89 ± 0.06	−4.361

* nZVI produced via Fe(II) reduction from a solution at a composition simulating the filtrate of Step III. ** The nZVI reaction was conducted in synthetic solution, as described in Table 1.

Under the tested experimental conditions, almost all the nitrate (typically above 90%) was reduced to TAN (Table 2). The results show unequivocally that TAN is the main nitrogen species product. Moreover, based on the results, it cannot be excluded that TAN was the exclusive end product and that no nitrogen gas was formed at all, since the ~10% difference observed between the initial NO_3^--N mass and the final NH_4^+-N mass fell within the measurement error.

Acid-base mass balance calculations were conducted in order to determine the percentages of nZVI that was oxidized to produce TAN, $H_{2(g)}$ and $N_{2(g)}$ (i.e., according to Equations (1), (8) and (9), respectively) at the various experimental conditions. To this aim, the concentrations of the dissolved products of these reactions were measured, and the acidity mass (i.e., H^+) required for maintaining a constant pH was recorded. In all of the experiments, the mass balance calculations showed that the reactions described by Equation (1) (reduction of nitrate to TAN) and Equation (8) (Fe oxidation by H^+) were the dominant, and likely the sole occurring reactions. The only exception were the pH 5–7 experiments, in which these reactions were the main ones, but possibly other minor reactions (see elaboration below) also took place. This finding corroborates the hypothesis that the main end product of nitrate reduction is TAN and that the product of oxidation of nZVI is dissolved Fe(II) rather than Fe(III). Mass balance calculations were conducted and their closure (in terms of percentage error) is shown in Table 2 (right hand column). An example of this calculation is presented herein, based on the results obtained in Experiment #2 (second row in Table 2): 3.28 mmol of TAN were measured at the end of the experiment. The initial NO_3^- mass was 3.57 mmol. It was assumed that 3.28 mmol of NO_3^- were reduced to TAN according to Equation (1). Since the molar ratio between TAN and Fe(II) in Equation (1) is 1:4, 3.28×4, i.e., 13.11 mmol of Fe(II) should have been produced through NO_3^- reduction. However, the Fe(II) mass measured at the end of the experiment was 25.99 mmol. Thus, it was assumed that 25.99–13.11, i.e., 12.88 mmol of Fe(II) resulted from iron oxidation by H^+, as described in Equation (8). According to this calculation 13.11 and 12.88 mmol of $Fe_{(s)}$ were oxidized according to Equations (1) and (8), respectively. Thus, in order to maintain a constant pH, 32.77 + 25.76 i.e., 58.53 mmol of H^+ should have been added to the solution, if indeed Equations (1) and (8) dominated. In practice, 57.81 mmol of H^+ were dosed in Experiment #2, i.e., a difference (or measurement error) of −1.25%:

$$5Fe_{(s)} + 12H^+ + 2NO_3^- \rightarrow 5Fe^{2+} + N_{2(g)} + 6H_2O. \tag{9}$$
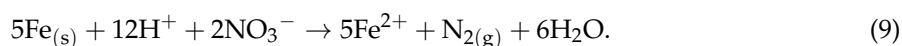
Another example can be given from the results of Experiment #6, in which 0.998 mmol of TAN were measured at the end of the experiment. The initial measured NO_3^- was 0.942 mmol. Assuming that TAN analysis is more accurate than nitrate analysis, and that TAN was produced via Equation (1), 3.99 (i.e., 0.998×4) mmol of Fe(II) should have been released. In this experiment, the measured Fe(II) mass was 4.02 mmol. That is, practically all the Fe(II) found in solution was a result

of the reaction described in Equation (1). Therefore, it was assumed that further Fe oxidation by H^+ (Equation (8)) did not take place. According to Equation (1) the stoichiometric ratio between NO_3^- reduced and H^+ consumed is 1:10; therefore, 9.98 meq of acidity were expected to be consumed to maintain constant pH, while 9.63 meq were actually dosed. Alternatively, since the stoichiometric ratio between Fe(II) formed and H^+ consumed is 0.4:1, 4.02/0.4 = 10.05 meq of acidity were expected to be consumed (a difference of ~4.2%). Table 2 shows that the deviations in all other experiments were also low (right hand side column). The Wilcoxon test results, applied to determine the likelihood that Equations (1) and (8) accounted solely for the observed results, suggested that the probability of calculated vs. observed differences being drawn from a distribution with zero median is 0.84. This value reflects a high probability that the experiments results were accounted solely by using the two considered reactions.

Examination of the mass balance errors (Table 2) suggests that at the (high) pH range of pH 5–7 other reactions also occurred, on top of Equations (1) and (8). This is demonstrated by the high error in the calculation of the anticipated supply of acidity in Experiment #4, (i.e., −12.15%). At this relatively high pH range, the likely explanation is that some Fe(II) precipitated according to Equation (10) to form ferrous hydroxide, a reaction which consumes OH^- ions, thereby reducing H^+ demand. The inevitable conclusion is that TAN is, to all practical intents and purposes, the only nitrogen end product of the reaction between nitrate and nZVI and that $N_{2(g)}$, which is often reported in this regard, does not form, at least not under the conditions investigated in this work:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_{2(s)} \tag{10}$$

To summarize, the results shown in Table 2 lead to the following conclusions: (a) TAN and Fe(II) are the main end products, resulting from Equations (1) and (8); (b) nZVI-enhanced nitrate reduction should be conducted at an acidic pH range, in which the nitrate reduction rate is higher. Accordingly, further work was conducted at pH 4 ± 1 (i.e., 3 < pH < 5). The reason was that at this pH range the oxidation rate of Fe(II) by residual O_2 is considerably slow [35], acid consumption for pH reduction is not excessive and also the rate of Fe(II) oxidation by H^+ is not very high.

### 3.2.2. Observed Reaction Rates

Our results showed, as expected, that the reactivity of the synthesized nZVI was slightly different from experiment to experiment. The minor differences in the reaction rate can reasonably be attributed to the differences in the nZVI reactivity rather than to the different conditions applied in each experiment. Nevertheless, the effect of pH and Cl^- concentration on the kinetics of nitrate reduction by nZVI were further studied. Figure 4 shows the evolution of N species with time under different experimental conditions. Evidently, no nitrate was detected in solution following five reaction minutes at the pH range 3–5, irrespective of the background Cl^- concentration (Figure 4a,b). In contrast, it took around 20 min for all the NO_3^- to be reduced at pH 5–7 (Figure 4c). Comparable findings were reported by Yang and Lee [17] who observed faster nitrate reduction at pH 2, 3 and 4, as compared to pH 5. It is noted, however, that the conditions in Yang and Lee [17]'s experiment were different, i.e., no background chloride concentration, lower initial nitrate concentration and higher Fe to NO_3^- ratio.

Dissolved Fe(II) profiles during the nZVI experiments are shown in Figure 5. "Total dissolved Fe(II)" reflects the measured amount of ferrous iron resulting from both nitrate and H^+ reduction while "Dissolved Fe(II) from nitrate reduction" represents the computed amount of Fe(II) resulting solely from nitrate reduction according to measured TAN and Equation (1). The difference between the total measured Fe(II) and calculated Fe(II) values (from NO_3^- reduction) emanates from nZVI reduction by H^+ (Equation (8)). At pH 3–5, the increase in the amount of Fe(II) resulting from nitrate reduction levelled off after five minutes, while the total dissolved Fe(II) mass constantly increased throughout the experiment (Figure 5a,b). This suggests that the reaction between nZVI and nitrate (Equation (1)) is faster than the reaction between nZVI and H^+ (Equation (8)) at pH 3–5. On the other hand, at pH 5–7,

the amount of dissolved Fe(II) resulting from nitrate reduction kept increasing throughout the duration of the experiment, indicating that the nitrate reduction rate is slower at pH 5–7 than that at the more acidic pH range. Thus, in order to complete the nitrate reduction at a short retention time, the pH value should remain below pH 5, which is also supported by the results shown in Figure 4c.
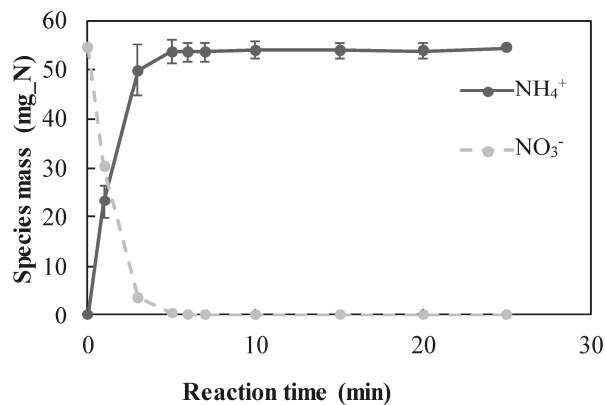
(**a**)
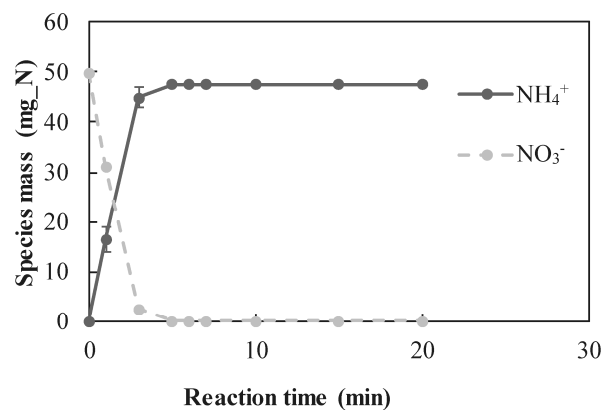
(**b**)
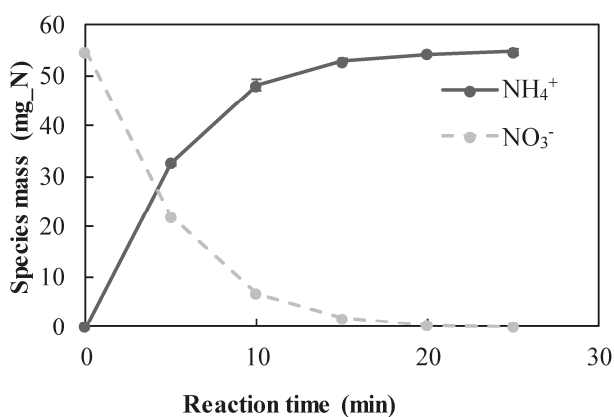
(**c**)

Figure 4. Average (*n* = 3 in most experiments) mass of nitrogen species during nitrate reduction by nZVI at various operational conditions: (**a**) pH 3–5; $[Cl^-]$ = 1.37 M; (**b**) pH 3–5; 0% Cl^-; and (**c**) pH 5–7; $[Cl^-]$ = 1.37 M. Shown nitrate concentrations were calculated based on TAN measurements.

As mentioned, at pH 3–5, no nitrate remained in solution after ~5 min under the investigated conditions. Thus, to minimize nZVI loss due to reaction with H⁺, nZVI particles should be separated from the solution after ~5 min of retention time at this pH range. Such separation may be done by applying a magnetic field or via filtration (both under anaerobic conditions). Such operation would minimize both acid and nZVI consumptions.
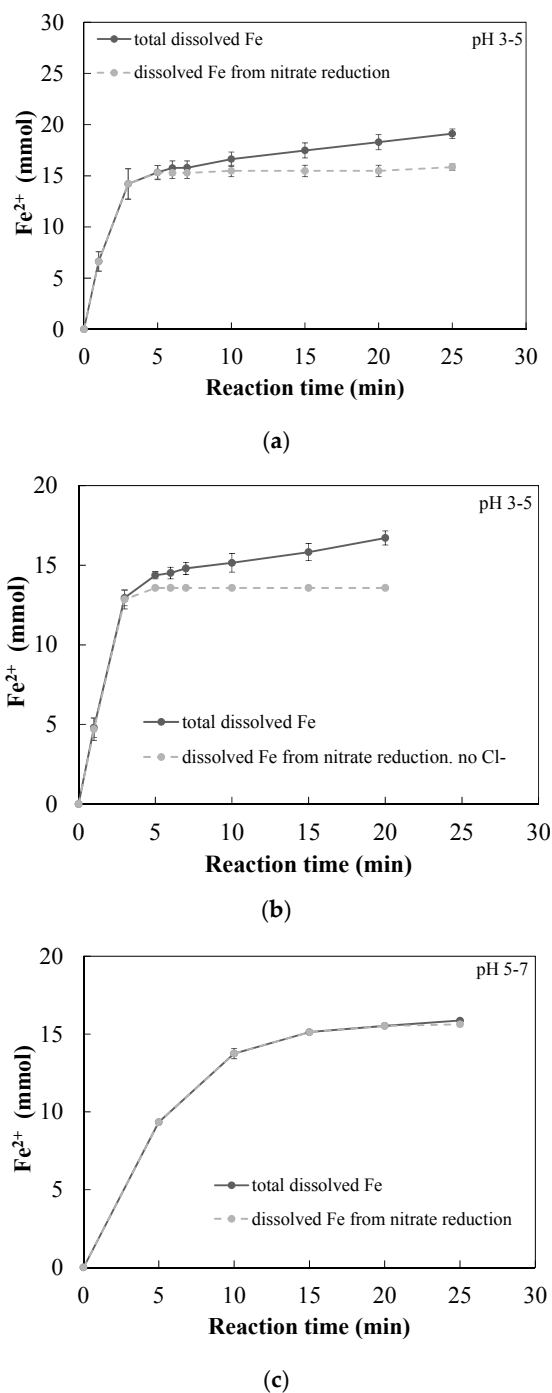

(**a**)

(**b**)

(**c**)

Figure 5. Fe(II) generation during nZVI enhanced nitrate reduction. (**a**) pH 3–5, $[Cl^-]$ = 1.37 M; (**b**) pH 3–5, 0% Cl^-; and (**c**) pH 5–7, $[Cl^-]$ = 1.37 M. "Total dissolved Fe" stands for measured Fe(II); Fe(II) resulting from nitrate reduction was computed using Equation (1).

3.3. Effect of Cl⁻ Ion Concentration on the Rate of Nitrate Reduction by nZVI

To examine whether a high Cl⁻ concentration has an effect on the nitrate reduction rate, the results obtained with high Cl⁻ background ([Cl⁻] = 1.37 M) were compared with results obtained in the absence of Cl⁻ (bottom row in Table 2). The differences in the evolution of dissolved Fe(II) and TAN concentrations, and of HCl consumption between the two cases, are observed by comparing Figure 4a,b, Figure 5a,b and Figure 6a,b, respectively. The results show that five minutes were sufficient for complete nitrate reduction in both cases, and no significant difference was observed as a result of the presence of high chloride concentration. These results seem to contradict the results presented by Choe et al. [26], which showed an acceleration effect on the reaction rate at high chloride concentration.
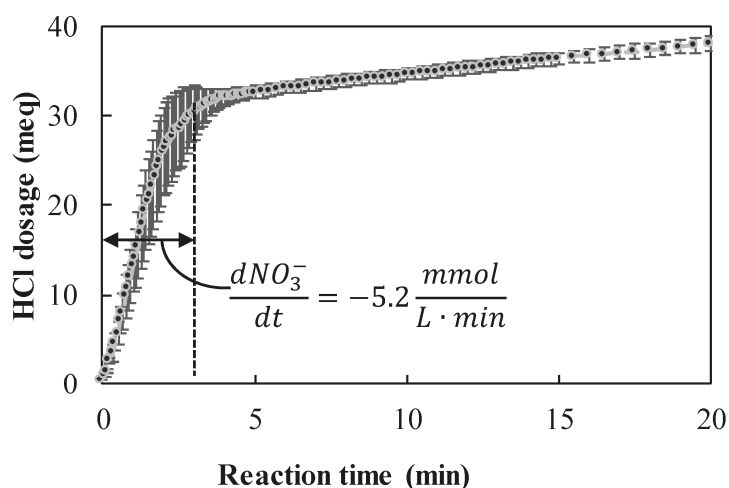

(**a**)
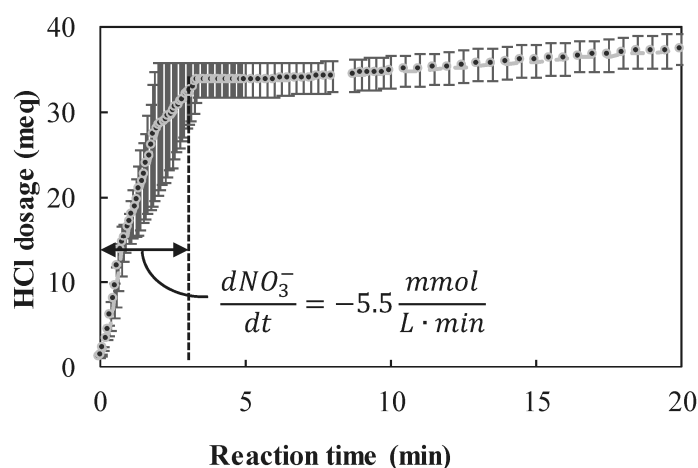
(**b**)

Figure 6. Acid consumption during nitrate reduction at pH 3–5 and different Cl⁻ concentrations: [Cl⁻] = 1.37 M and 0 M, (**a**) and (**b**), respectively.

Figure 6 shows the HCl consumption during the nZVI nitrate reduction experiments. Figure 6 shows two clear linear HCl consumption trends with time. The two linear slopes imply that different reactions took place at two different time intervals. This observation is also supported by the results shown in Figures 4a,b and 5a,b: during the first five minutes, the dominant reaction was nitrate reduction by nZVI (Equation (1)). Thereafter, upon the disappearance of NO_3^-, acid was consumed due to the reaction between Fe and H^+ (Equation (8)). Focusing on the nitrate reduction in the first

three minutes, no significant difference was observed between the reaction rate calculated from the results of the two experiments (i.e., at high and at zero Cl^- concentrations, Figure 6a,b, respectively). In the high Cl^- concentration scenario, the nitrate removal rate according to HCl consumption was 5.22 mmol NO_3^- L^{-1} min^{-1} ($R^2 = 0.956$), as compared to 5.52 mmol NO_3^- L^{-1} min^{-1} ($R^2 = 0.912$) in the nil Cl^- scenario. Calculating the nitrate removal rate based on measured TAN concentrations (Figure 4a,b) during the first three minutes yielded 5.50 and 4.78 mmol NO_3^- L^{-1} min^{-1} ($R^2 = 0.969$ and $R^2 = 0.998$), at high chloride and nil chloride concentrations, respectively. In both cases, the nitrate reduction reaction followed a zero order rate. The more accurate result was probably attained by the calculations based on acid consumption, since its resolution was higher than the measured TAN concentrations. In any event, it was evident that the presence of high chloride concentrations did not affect the nitrate reduction rate in a significant manner, and it can be thus concluded that the high Cl^- presence does not detract from the attractiveness of the proposed process.

3.4. Effect of nZVI Excess over the Stoichiometric Ratio

In most of the works that focus on iron as nitrate reducing agent, an excess iron mass (in the range of 2.7 to 14 times higher than the stoichiometric ratio defined by Equation (1)) was applied (e.g., [14,17,20,24]). An experimental investigation of the effect of the excess nZVI dosage was conducted in this work by comparing the results obtained from two experiments differing in the mass of Fe dosed: first, the Fe mass was three times higher than required according to stoichiometry; next, a 10% excess over the stoichiometric ratio was dosed (Figure 7). The results showed that applying nZVI in large excess has a marked effect on the reaction rate: in the 10% excess experiment, around 25 min were required for nitrate to be reduced to TAN. The nitrate reduction rate (during the first seven minutes), calculated based on acid consumption, was 1.81 mmol NO_3^- L^{-1} min^{-1} ($R^2 = 0.995$). The rate based on TAN formation was similar: 1.87 mmol NO_3^- L^{-1} min^{-1} ($R^2 = 0.991$). That is, the rate at the 10% Fe excess was around three times slower than the rate when the Fe dosage was three times higher than the stoichiometric ratio. Mass balance calculations showed again that, under both scenarios, the same two reactions (i.e., Equations (1) and (8)) were dominant. Since the nZVI particles are separated and reused in the proposed process (Figure 1), it is clearly advantageous to operate the process with nZVI in considerable excess, thereby increasing the nitrate reduction rate and minimizing reactor size.
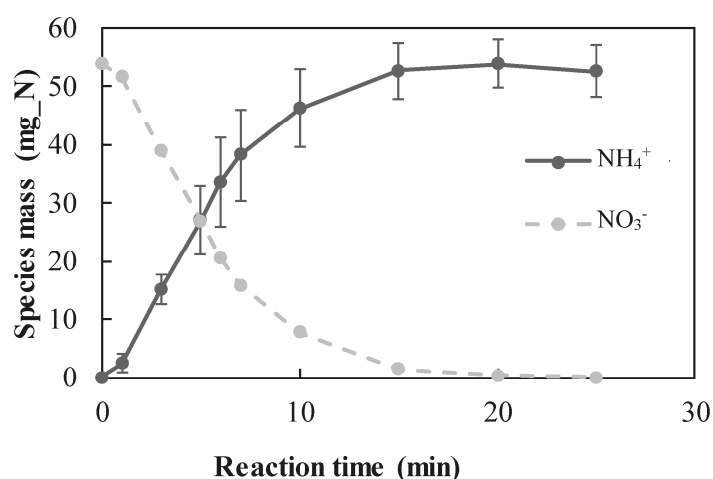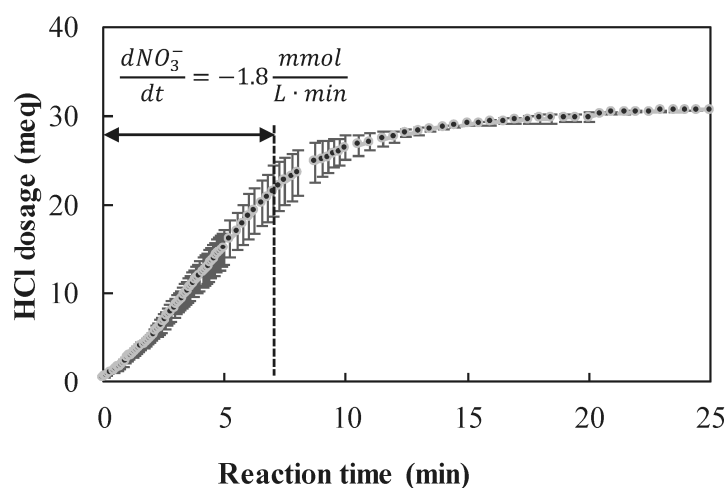

(a)

Figure 7. *Cont.*
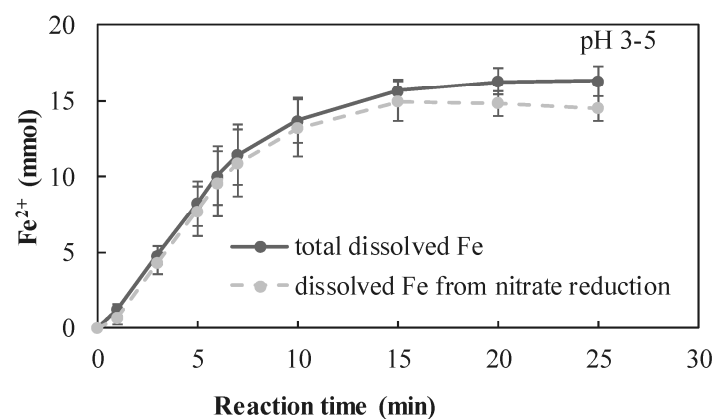
(b)

(c)

Figure 7. Results of nZVI enhanced nitrate reduction at pH 3–5 and 1.37 M Cl⁻ concentration, nZVI dosage at 10% above the stoichiometric ratio: (**a**) nitrogen species mass (the shown nitrate concentrations were calculated based on TAN measurements); (**b**) Fe(II) mass; (**c**) acid consumption.

3.5. Synthesizing nZVI from the Solution Resulting from the Nitrate Reduction Step

The feasibility of the overall process (Figure 1) depends also on the ability to re-synthesize nZVI from the inherent dissolved Fe(II). Re-synthesizing nZVI from the NaCl brine following step III is imperative, for several reasons: (1) it enables recycling the NaCl brine in the next IX regeneration steps; (2) it eliminates the need to add ferric chloride to the process; and (3) it enables applying Step V (Figure 1) without the formation of ferric ion (which would result from Fe(II) electrooxidation), which might subsequently precipitate as $Fe(OH)_3$ on the cathode. To protect the cathode from scaling, it is necessary to separate dissolved iron from the solution prior to introducing it into the electrochemical chamber. Such separation can be achieved by reducing Fe(II) to nZVI that can be subsequently filtered out of the solution. Note that filtration of nZVI is an inherent step of the nZVI production procedure.

The nZVI produced using the solution leaving the nitrate reduction step (i.e., produced at the presence of ammonium, chloride, sodium and from Fe(II)) appeared visually similar to the nZVI produced from the fresh ferric solution. The efficiency of this step was determined first by measuring the dissolved Fe(II) found in the filtrate of the synthesis. The percentage of the Fe(II) that did not react to form nZVI was quantified and shown to amount to less than 0.02% of the

initial Fe(II) concentration, making the efficiency of this step very high. To further confirm the reactivity of the nZVI and its effectiveness within the process, the formed nZVI particles were used for nitrate reduction under experimental conditions identical to those conducted with the nZVI particles prepared from a pristine ferric solution. Nitrate was completely reduced to TAN using the reproduced nZVI (Experiment #6, Table 2). The normalized Fe(II) concentration (Table 2) obtained in this experiment (after 28 min) was lower than the concentrations recorded in two similar experiments (Experiments #5 and #7). The total dissolved Fe(II) and the computed Fe(II) resulting solely from NO_3^- reduction were practically identical in Experiment #6, indicating minimal Fe oxidation by H^+. However, as mentioned before, minor differences in nZVI reactivity could also be attributed to slight differences in the synthesis procedure.

It is noted that the method used for production of nZVI involves the accumulation of boric acid in the NaCl brine (see Equation (7)) due to the use of borohydride. Boric acid is an inert species in the IX step, as it probably is also during Steps III, IV and V. However, this effect (if apparent) was not examined in the current work. In case the accumulation of the $B(OH)_3$ in the solution is found to be detrimental, fresh NaCl solution must be prepared following each 5–6 regeneration cycles. Since the regeneration solution has to be discarded periodically, the overall process efficiency is somewhat lower than the combination of efficiencies of each individual step. Overall, it can be shown that approximately 78% of the NaCl is recovered. This figure includes the ~1.5% loss of chloride in the ion-exchange step in which chloride replaces nitrate (and to a lesser extent also other anions). Finally, brine discharge is minimized by a factor of five.

3.6. TAN Electrooxidation Step

In order to recycle the filtrate (following re-synthesis of the nZVI particles) for another IX-nZVI cycle, its TAN concentration should be considerably reduced.

The results of the electrooxidation experiments at the chosen conditions (current density = 267 A/m^2) are shown in Figure 8, which shows that, after ~90 min, practically all of the TAN was oxidized to nitrogen gas at a current efficiency of 86.2%. The main apparent reasons for the deviation from 100% efficiency were O_2 formation at the anode which competed with Cl_2 formation for the supplied electrons, nitrate formation at the anode and simultaneous nitrate and chlorine species reduction at the cathode [36].
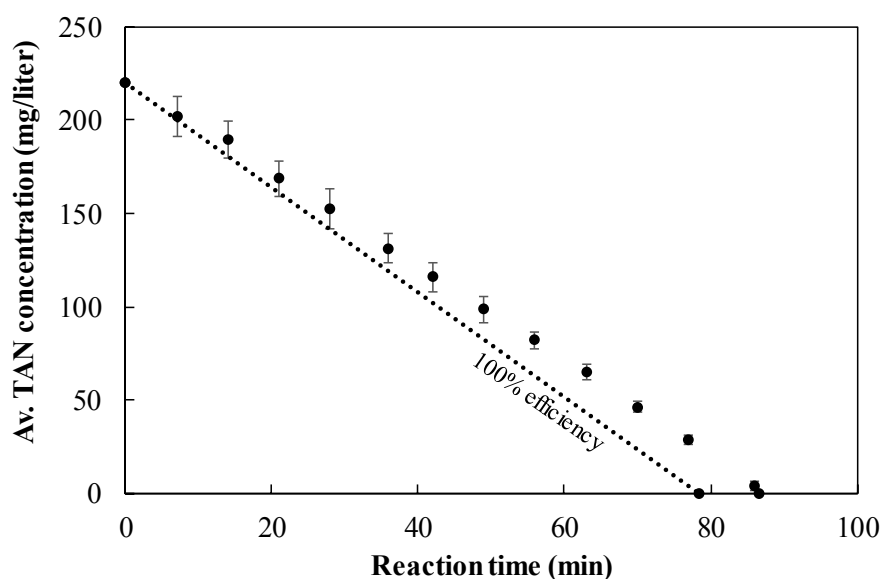

Figure 8. Average TAN concentrations (*n* = 3; error bars indicate standard deviation) as a function of time during the electrolysis experiments (room temperature, current density 267 A/m^2).

Considering the proposed process sequence, at the end of the electrolysis step, Na_2SO_3 should be dosed to the water to reduce residual chlorine species back to Cl^-, thereby preventing Cl_2 from damaging the IX resin. Another possible option is to control the electrolysis step to stop before all of the ammonium is oxidized, since a small residual amount of TAN would not significantly affect the following IX step.

4. Conclusions

- A new process for treating nitrate-polluted drinking water, consisting of anionic exchange followed by nano Fe-induced NO_3^- reduction and TAN electrooxidation, was described. The process consists of five steps and applies three different technologies: ion-exchange, chemical reduction by nZVI and electro-oxidation. In these steps, nitrate is separated from the polluted water, reduced to TAN at low pH, and, finally, TAN is oxidized into nitrogen gas. This sequence, plus a step in which new n-ZVI is generated from the effluent solution of the nitrate reduction step, allows reusing the regeneration solution for many cycles. A significant advantage of the presented process is that the chemical treatment is not carried out directly on the drinking water, making post treatment redundant. The process is sustainable in the sense that the end product is benign $N_{2(g)}$, the chemicals used (NaCl and nZVI) and also water are mostly (~80%, ~100% and ~80%, respectively) recovered and brine disposal is minimized by a factor of 5.

- ~80% of the main process commodities are recycled, resulting in a significant improvement over conventional IX processes, which neither recover brine nor reduce the disposed volume. Similarly, conventional nitrate reduction using nZVI is not accompanied by any Fe(II) recovery and TAN removal, as applied in the current process.

- A new approach for quantitative determination of the dominant reactions in nitrate reduction by nZVI was applied. The method is based on the measuring nitrogen species, dissolved Fe(II) concentrations, and acid consumption for maintaining constant pH. The data was analyzed using mass balance calculations and tested statistically to test its compatibility with previously published reactions. The Wilcoxon test was used to determine that only two reactions were dominant at acidic pH range, i.e., $4Fe_{(s)} + 10H^+ + NO_3^- \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O$ and $Fe_{(s)} + 2H^+ \rightarrow Fe^{2+} + H_{2(g)}$. Thus, the notion appearing in a few works, that NO_3^- is partly reduced by nZVI to $N_{2(g)}$, was disproved.

- Distinct operational conditions (corresponding to the expected characterization of ion-exchange regenerant solution) were tested for conducting the chemical reduction of nitrate by nZVI: high Cl^- concentrations of 45 g Cl^-/L along with high nitrate concentrations of 250 mg N/L. The effect of the presence of high Cl^- concentration was found not to inhibit the nitrate reduction rate, implying that the use of nZVI for nitrate reduction within concentrated brines is feasible. Large excess of nZVI was found to increase the nitrate reduction rate compared to operation at close to stoichiometric ratio. In the proposed process, applying excess nZVI does not affect the economic feasibility, since the nZVI can be collected and reused.

- A drawback of the proposed process that should be addressed in future work relates to the removal of by-products from the nZVI synthesis procedure (e.g., $B(OH)_3$), which may accumulate in the regenerant solution if not separated at predetermined intervals.

- The nZVI enhanced nitrate reduction was found to follow a zero order rate, with a rate coefficient of ~5 mmol NO_3^- L^{-1} min^{-1} when nZVI was in high excess and ~1.8 mmol NO_3^- L^{-1} min^{-1} when nZVI was only slightly above the stoichiometric dose.

Author Contributions: For research articles with several authors, a short paragraph specifying their individual contributions must be provided. The following statements should be used Inbal Fux, Liat Birnhack and Ori Lahav conceived and designed the experiments; Inbal Fux and Samuel C.N. Tang performed the experiments; All authors

analyzed the data and contributed to the writing of the paper. Authorship must be limited to those who have contributed substantially to the work reported.

Conflicts of Interest: The authors declare no conflict of interest.

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