Int. J. Environ. Sci. Technol. (2014) 11:1733–1742
DOI 10.1007/s13762-013-0375-0

ORIGINAL PAPER

Nitrate removal from water using UV-M/$S_2O_4^{2-}$ advanced reduction process

N. Bensalah · R. Nicola · A. Abdel-Wahab

Received: 2 October 2012 / Revised: 7 April 2013 / Accepted: 8 September 2013 / Published online: 3 October 2013

Abstract In this work, a new process called advanced reduction process (ARP) was used for nitrate removal from water. This ARP process combines sodium dithionite as reducing agent with ultraviolet irradiation using medium pressure lamps (UV-M) as an activating method. Experimental results showed that UV-M/$S_2O_4^{2-}$ process achieved almost complete removal of nitrate from aqueous solutions containing 25 mg NO_3^-/L using stoichiometric dose of dithionite of 68.8 mg/L at neutral pH conditions. Analysis of final products and material balance confirmed that NO_3^- ions were reduced to ammonium with formation of nitrite as intermediates in addition to the formation of small amounts of volatile species, mainly ammonia and nitrogen gas. Effects of certain experimental parameters including dithionite dose, initial pH, initial nitrate concentration, and UV light source on the kinetics and efficiency of nitrate reduction were evaluated. Increasing dithionite dose augmented the rate of nitrate reduction and enhanced the efficiency of ARP process. Dithionite doses higher than stoichiometric ratios led to complete removal of nitrate in shorter reaction time. UV-M/$S_2O_4^{2-}$ process was found to be effective only under neutral pH or alkaline conditions, and its removal efficiency is negligible in acidic medium ($pH < 4$). Irradiation with UV-M was more effective than low pressure or narrow band lamps. These results can be attributed to the contribution of several mechanisms for nitrate reduction to ammonium. These include the following: direct photolysis, chemical reduction of nitrate dithionite, and mediated reduction of nitrate by free reducing radicals.

Keywords Nitrate reduction · Advanced reduction processes · UV-M irradiation · Dithionite · Reducing radicals

Introduction

Nitrate (NO_3^-) is one of the most widespread contaminants of ground water, due to its use as a fertilizer and its formation from other nitrogen forms in human and animal wastes. Also, it is naturally present in surface water resources at low levels due to the liquid–gas equilibrium between the water and air (Burow et al. 1998; Nolan and Hitt 2006; Rivett et al. 2008; Rupert 2008, Kundu and Mandal 2009). Additionally, industrial wastewater discharges from industries such as pharmaceutical industry, oil and gas industry, and nuclear fuel processing industry are major sources of NO_3^- contamination (Burow et al. 2010, Puckett et al. 2008). Furthermore, improperly designed and installed sewer systems that may encounter failures or leaks as well as septic systems are also considered a major source of NO_3^- since they release nitrogen-rich waste to soil and groundwater.

Nitrate (NO_3^-) can cause severe disruption to human health and the environment (Tsezou et al. 1996; Gupta et al. 2000; Fan and Steinberg 1996; US EPA 2006, 2007). Ingestion of large quantities of NO_3^- incapacitates the human's red blood cells as oxygen carriers leading to a fatal condition of methemoglobinemia, commonly referred to as "Blue Baby Syndrome" (Sanchez-Echaniz et al. 2001; Greer and Shannon 2005). It can also have

N. Bensalah (✉)
Department of Chemistry and Earth Sciences, College of Arts and Science, Qatar University, PO Box 2713, Doha, Qatar
e-mail: nasr.bensalah@qu.edu.qa

R. Nicola · A. Abdel-Wahab
Chemical Engineering Program, Texas A&M University at Qatar, PO Box 23874, Education City, Doha, Qatar

carcinogenic effects on humans (Preston-Martin et al. 1996; George et al. 2001; Volkmer et al. 2005). Similar effects were noted on the aquatic life as fish that inhale water of high NO_3^- concentrations (>10 mg/L) also suffer lack of oxygen in the blood in a condition named "Brown Blood" (Knobeloch et al. 2000). The presence of high NO_3^- concentrations generally damages the aquatic life since it stimulates reactions that consume oxygen in the water, leading to oxygen depletion.

Several treatment methods have been used for nitrate removal from water. NO_3^- removal using chemical reduction to nitrite and then to ammonia or nitrogen gas is gaining interest because of its high efficiency and cost-effectiveness (Fanning 2000). Some of the reagents that have been used are active metals. Methods include the addition of the metal in powder form to the solution (Murphy 1991; Huang et al. 1998; Pintar et al. 2001; Huang and Zhang 2004; Yang and Lee 2005; Liou et al. 2009) or setting up in a circuit to reduce NO_3^- electrochemically (Katsounaros et al. 2006; Ghafari et al. 2008; Li et al. 2010). Use of active metals, however, showed many limitations in both forms; this is because they can only reduce small quantities of NO_3^- and deliver a mixture of ammonia, nitrogen, and nitrite, which is undesired. Different metals also work strictly under certain controlled pH conditions and may require low or elevated temperatures. Additionally, metal consumption is economically unattractive. Another reducing agent is ammonia which can reduce NO_3^- to nitrogen and nitrous oxide under elevated temperatures and pressures (Dell'Orco et al. 1997). This reaction is difficult to control and is associated with many safety concerns. Borohydride is another reagent that has been studied and proven to reduce NO_3^- under neutral or basic conditions but it requires the addition of catalysts such as Cu or Zn (Fanning et al. 2000). Formate and organic substances were also tested to form complex reactions that require the presence of initiators and catalysts (Bludenko et al. 2002). Organic compounds (e.g., methanol) were used to reduce NO_3^- through a photochemical process but NO_3^- removal was only achieved under very high temperatures and pressures (Sato et al. 1996). Hydrazine and hydroxylamine are reducing agents that burn rapidly in the presence of a salt catalyst to reduce NO_3^- to nitrite (Silva et al. 2007). This process is not attractive due to its safety hazards and catalyst consumption. Hydrogenation reactions at low pressure and in the presence of Cu–Pd bimetallic catalysts can reduce NO_3^- to nitrogen (Barrabes et al. 2006; Marchesini et al. 2008; Soares et al. 2011). This reaction has limited reduction rate due to the difficulty of keeping H_2 in solution. Iron (II) is another agent that can reduce both nitrate and nitrite. Maximum removal of 93 % was noted under helium atmosphere with a Cu (II) catalyst (Ottley et al. 1997). All of the aforementioned methods have limitations either with removal efficiency, slow rate, cost–effectiveness, or safety hazards which make them unattractive for nitrate removal.

A new group of treatment processes that is based on producing highly reactive reducing radicals that can destroy oxidized contaminants by chemical reduction has been recently developed by our research group. These treatment methods are called advanced reduction processes (ARPs) and combine a reductant and activating method to produce highly reactive reducing free radicals. Dithionite ions ($S_2O_4^{2-}$) are promising reductants for application in ARPs, because they have a weak S–S bond, which can be easily broken by activating methods into sulfur dioxide radical anions ($SO_2^{\bullet -}$) (Hodgson et al. 1956; Rinker et al. 1959; Wasmuth et al. 1964; Yang et al. 2007). Dithionite ions absorb ultraviolet light at 315 nm which indicates that UV irradiation can provide enough energy to promote formation of $SO_2^{\bullet -}$ reducing radicals.

Dithionite is a high production volume chemical, primarily because of its industrial use in bleaching wood pulp (Dence 1996; Ellis 1996; Lindholm 1999; Pemberton, et al. 1995) and its use in dyeing textiles, which helps to maintain its relatively low price of $0.76/lb (The Innovation Group 2008). In addition to its industrial uses, dithionite is widely used by soil scientists to reductively extract iron from soils (Gan et al. 1992). The ability to reduce iron has also been applied to developing in situ aquifer remediation technology where iron in aquifer solids is reduced by dithionite and the reduced iron subsequently reduces oxidized contaminants (Szecsody et al. 2004; Ludwig et al. 2007).

The purpose of this research work was to investigate the reduction of nitrate by ARPs that combines UV irradiation using medium pressure lamps (UV-M) emitting light in the range of 200–600 nm with dithionite ions (UV-M/$S_2O_4^{2-}$). The effects of certain experimental parameters on the kinetics and efficiency of nitrate reduction were evaluated. An empirical kinetic model that describes the rate of nitrate reduction was developed.

The current study was carried out at laboratory of Environmental Engineering, Department of Chemical Engineering at Texas A&M University at Qatar, Doha, Qatar, during the period from January 2012 to June 2012.

Materials and methods

Chemicals

Sodium nitrate ($NaNO_3$) and sodium nitrite ($NaNO_2$) were analytical grade chemicals (purity >99 %) purchased from Sigma-Aldrich and Fluka. Sodium hydrosulfide ($Na_2S_2O_4$) of purity over 82 % was provided by Sigma. The other chemicals such as sulfuric acid, sodium hydroxide, sodium phosphate, ammonium sulfate were of analytical grade and were provided by Sigma-Aldrich or VWR. All solutions were prepared with deionized deoxygenated water (DDW) obtained from a Milli-Q system, with resistivity >18 MΩ cm at 25 °C and purged with nitrogen gas.

Analytical methods

The analyses of nitrate and nitrite were performed by ion chromatography using Dionex ICS-2000 ion chromatograph. The chromatograph was equipped with AS autosampler, IonPac AG19 guard column (4 × 50 mm), IonPac AS19 separation column (4 × 250 mm), ASRS 300-4 mm suppressor, DS6 conductivity cell, and eluent generator (EGC). The mobile phase was 20 mmol/L (mM) aqueous solution of potassium hydroxide (KOH) at a constant flow rate of 1 mL/min, and it was prepared manually or automatically with EGC. Standard solutions of nitrate and nitrite were prepared by dilution of stock solutions to concentrations ranging from 1 ppm to 100 mg/L. All calibration curves were linear with correlation coefficients (R^2) higher than 0.99. Method accuracy and precision were determined by measuring seven replicates at two levels. Total nitrogen (TN), nitrate/nitrite Nitrogen (NN), and Total Kjeldahl Nitrogen (TKN) were monitored using Skalar Formacs^{HT} TOC/TN analyzer. The pH was measured by VWR pH meter (model SympHony).

Experimental procedures

Batch experiments were conducted to determine the kinetics of nitrate reduction by UV-M/$S_2O_4^{2-}$ process. All solutions were prepared with deionized and deoxygenated water (DDW) under anaerobic conditions assured by a flexible vinyl anaerobic chamber (Coy Laboratory Products Inc., USA) filled with 99.99 % nitrogen and equipped with an oxygen and hydrogen analyzer, fan boxes and palladium catalyst STAK-PAK. To prepare DDW, deionized water was purged with 99.99 % nitrogen (or argon) for 2 h and kept in the anaerobic chamber overnight until use. All experiments were performed in duplicate in 17 mL quartz cells (Starna 32/Q/10, Spectrosil® Quartz) with 10 cm optic path length and fitted with PTFE stopper. UV irradiation was conducted using medium pressure mercury lamp (TQ150, UV-consulting Peschl, Germany) emitting polychromatic UV light between 200 and 600 nm with a power input of 150 W. During UV-M irradiation experiments, quartz cells containing a mixture of nitrate and dithionite, and UV lamp were enclosed in a box to ensure safe operation and to prevent exposure to extraneous light. The beam was parallel, and the distance between lamp and the cells was adjustable to control the light intensity. The lamp was warmed up for 10 min to reach constant output, and then irradiation experiments started. Samples were taken after the desired reaction time and immediately analyzed for the target compound(s).

In order to verify the efficacy of combining UV-M and dithionite, nitrate reduction using dithionite alone and UV-M alone was also tested.

Results and discussion

Preliminary experiments were conducted at room temperature and under neutral pH to evaluate the viability of the UV/dithionite process. Figure 1 presents the changes of nitrate concentration with time during the treatment of aqueous solution containing 25 mg/L nitrate by UV-M irradiation alone, chemical reduction with $S_2O_4^{2-}$ ions, and combined UV-M/$S_2O_4^{2-}$ system. Stoichiometric amount of dithionite (68.8 mg/L) was used assuming that nitrate is reduced to ammonia and dithionite is oxidized to sulfate according to the following Eq. (1):

$$3NO_3^- + 4S_2O_4^{2-} + 7H_2O \rightleftarrows 3NH_3 + 8SO_4^{2-} + 5H^+ \tag{1}$$

As it can be seen, UV-M irradiation alone and chemical reduction with $S_2O_4^{2-}$ ions removed around 18 % and 10 % of nitrate after 240 min, respectively. However, the combination of UV irradiation with $S_2O_4^{2-}$ ions, under same operating conditions, resulted in complete removal of nitrate.

These results can be interpreted as follows:

- Direct photolysis of nitrate ions by UV-M irradiation can cause a decrease in nitrate concentration through the production of nitrites ions and oxygen according to the following reaction (2):

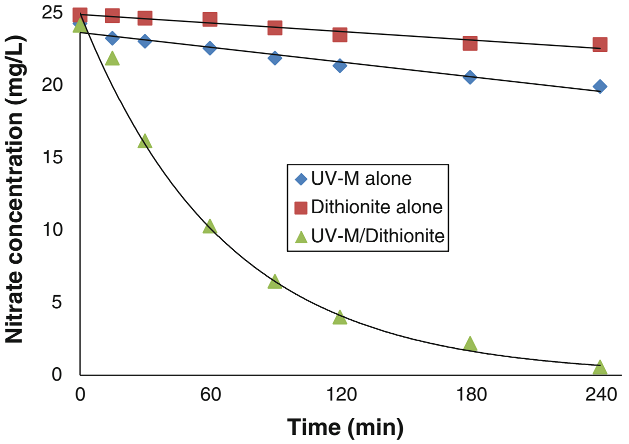

Fig. 1 Changes of nitrate concentration with time during the treatment of nitrate aqueous solutions by UV-M alone, dithionite alone, and UV-M/$S_2O_4^{2-}$ system. Experimental conditions: *nitrate* 25 mg/L, *dithionite* 68.8 mg/L, *UV light intensity* 2,400 ± 10, room temperature (22–23 °C), pH 7 (phosphate-buffered solution)

$$2NO_3^- + h\nu \rightleftarrows 2NO_2^- + O_2 \tag{2}$$

- Water radiolysis by UV light can also produce reductive and oxidative free radicals as given by reaction (3):

$$H_2O \rightleftarrows H^{\cdot} + OH^{\cdot} \tag{3}$$

These radicals can participate in reducing nitrate concentration.

- It is well known that $S_2O_4^{2-}$ ions are highly reductive species in water. These ions can react with nitrate ions and reduce them, but they are not powerful enough to completely transform them into highly reduced forms.
- Dithionite irradiated with UV-M produces sulfur dioxide anion radicals ($SO_2^{\bullet -}$) (called also sulfoxyl radicals) by homolytic rupture of the weak S–S bond of $S_2O_4^{2-}$. These instable and powerful reducing radicals react rapidly with nitrate and completely remove them from water.

Figure 2 shows final nitrate, nitrite, and N-intermediates concentrations with time during the treatment of aqueous solution containing 25 mg/L nitrate by UV-M/$S_2O_4^{2-}$ system using 68.8 mg $S_2O_4^{2-}$/L under neutral pH condition (pH = 7.0). The results presented in Fig. 2 showed that nitrate is almost completely removed from the solution after 240 min UV-M/$S_2O_4^{2-}$ reaction time. Nitrite was identified as the main intermediate of nitrate reduction. Nitrite concentration increased rapidly at the beginning of the treatment, and then, it reached a maximum at 90 min, after that it decayed till the end of the experiment.

Total nitrogen (TN), nitrate/nitrate nitrogen (NN), total Kjeldahl nitrogen (TKN), and volatile nitrogen (VN) (calculated by mass balance) for the same experiment are presented in Fig. 3. NN decreased rapidly and linearly with time, while TKN increased with time. These results indicate that nitrate and nitrite were reduced into ammonium ions (NH_4^+) during UV-M/$S_2O_4^{2-}$ treatment. TN decreased rapidly during the first 60 min and then decreased slowly for the rest of reaction time. The decrease in TN during the experiment indicates the formation of volatile nitrogen intermediates such as ammonia (NH_3) and nitrogen gas (N_2). Ion chromatography and TOC/TN results confirmed that ammonium ions are the major final products of nitrate reduction with UV-M/$S_2O_4^{2-}$ ARP system with formation of nitrite ions as intermediates.

These experimental results demonstrated that the UV/$S_2O_4^2$ process can be applied effectively to reduce nitrate into ammonium and nitrogen gas in neutral conditions. The efficiency of this process is related to the formation of powerful reducing free $SO_2^{-\bullet}$ radicals and other reducing species produced by photodecomposition of $S_2O_4^{2-}$ ions by UV-M irradiation as given in the following Eqs. (4, 5, 6).

$$S_2O_4^{2-} + h\nu \rightleftarrows 2SO_2^{-\cdot} \tag{4}$$

$$SO_2^{-\cdot} + H_2O \rightleftarrows SO_3^{2-} + H^{\cdot} + H^+ \tag{5}$$

$$2H^{\cdot} \rightleftarrows H_2 \tag{6}$$

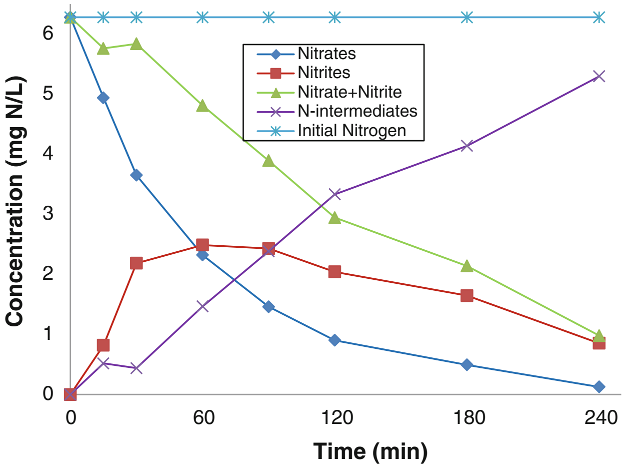

Fig. 2 Changes of nitrogen species concentrations with time during UV-M/$S_2O_4^{2-}$ treatment of nitrate aqueous solutions. Experimental conditions: *nitrate* 25 mg/L, *dithionite* 68.8 mg/L, *UV light intensity* 2,400 ± 10, room temperature (22–23 °C), pH 7 (phosphate-buffered solution)

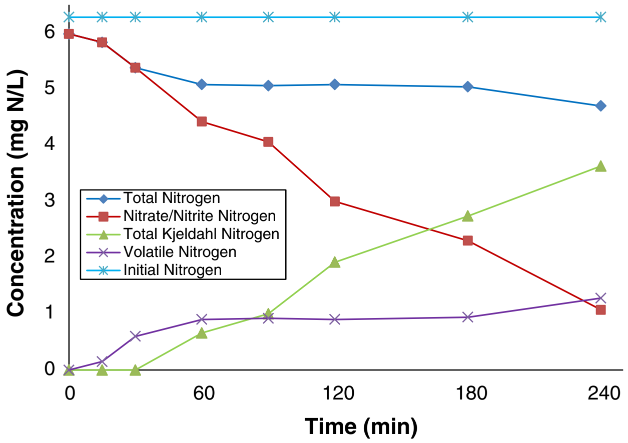

Fig. 3 Changes of TN, NN, and TKN with time during UV-M/$S_2O_4^{2-}$ treatment of nitrate aqueous solutions. Experimental conditions: *nitrate* 25 mg/L, *dithionite* 68.8 mg/L, *UV light intensity* 2,400 ± 10, room temperature (22–23 °C), pH 7 (phosphate-buffered solution)

Effects of certain experimental parameters including dithionite dose, initial pH, UV light, and initial nitrate concentration on the rate and efficiency of UV-M/$S_2O_4{}^{2-}$ ARP process should be optimized to maximize rate and efficiency of nitrate removal from water with reasonable doses of reducing agent and reasonable energy requirements.

The initial concentration of dithionite determines the efficiency of UV-M/$S_2O_4{}^{2-}$ process as dithionite is the source of free reducing radicals involved in the mechanism of nitrate reduction and formation of intermediates. Effect of $S_2O_4{}^{2-}$ dose on nitrate removal was evaluated at constant pH (7.0), temperature (23–25 °C), and initial nitrate concentration (25 mg $NO_3{}^-$/L). $S_2O_4{}^{2-}$ dose was varied from 14.1 to 227 mg/L. Figure 4 presents the effect of $S_2O_4{}^{2-}$ dose on nitrate reduction with time. The increase in dithionite concentration enhanced both kinetics and efficiency of nitrate reduction. Nitrate removals of 66 and 86 % were obtained for 14.1 and 28.2 mg/L dithionite, respectively. However, more than 99.9 % of nitrate was removed for dithionite dose of ≥68.8 mg/L which corresponds to (dithionite-nitrate) stoichiometric ratio of ≥4:3. Results shown in Fig. 4 indicate that the kinetics of nitrate reduction by UV-M/$S_2O_4{}^{2-}$ system follows a pseudo-first-order reaction regardless of initial dithionite concentration in the range of 10–250 mg $S_2O_4{}^{2-}$/L. Thus, the kinetics of nitrate reduction by UV-M/$S_2O_4{}^{2-}$ process can be described by the following simplified empirical pseudo-first-order equation:

$$-\frac{\mathrm{d}[\mathrm{NO}_3^-]}{\mathrm{d}t} = k_{\mathrm{app}}[\mathrm{NO}_3^-] \qquad (7)$$

where [$NO_3{}^-$] is the concentration of nitrate after reaction te "t", k_{app} is the apparent rate constant of nitrate reduction.

According to this hypothesis, the rate equation can be integrated considering the boundary conditions $[\mathrm{NO}_3^-] = [\mathrm{NO}_3^-]_{t=0}$ for t = 0 and $[\mathrm{NO}_3^-] = [\mathrm{NO}_3^-]_{t=t}$ for t=t, leading to the following equation:

$$[\mathrm{NO}_3^-]_{t=t} = [\mathrm{NO}_3^-]_{t=0}\mathrm{e}^{-k_{\mathrm{app}}.t} \qquad (8)$$

The experimental data fittings of $[\mathrm{NO}_3^-]_{\mathrm{t=t}}$ versus time (t) at different $S_2O_4{}^{2-}$ doses using Eq. (8) are presented in Fig. 4 and they show that the pseudo-first-order kinetics can accurately predict the rate of nitrate reduction by UV-M/$S_2O_4{}^{2-}$ with correlation coefficient (R^2) higher than 0.98. Figure 5 presents the variation of k_{app} with initial dithionite concentration in the range 10–250 mg $S_2O_4{}^{2-}$/L. The profile of calculated k_{app} values versus dithionite concentration suggests that the rate constant of nitrate reduction by UV-M/$S_2O_4{}^{2-}$ process increases linearly with the increase in dithionite dose.

Based on the results shown in Figs. 4 and 5, it appears that initial $S_2O_4{}^{2-}$ concentrations higher than 68.8 mg/L do not markedly enhance efficiency of UV-M/$S_2O_4{}^{2-}$ process. The influence of the initial $S_2O_4{}^{2-}$ dose can be explained as follows:

- For low $S_2O_4{}^{2-}$ doses, the amount of $SO_2^{-\bullet}$ radicals generated by UV irradiation of dithionite ions is not high enough to totally remove nitrate from water (Drozdova et al. 1998; Liu et al. 2011).

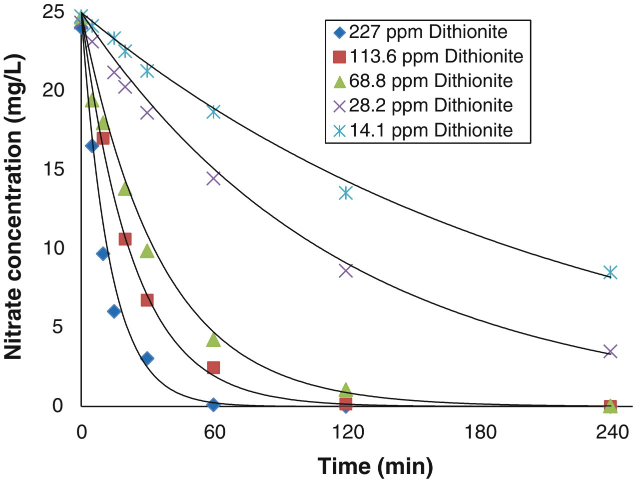

Fig. 4 Influence of dithionite dose on the kinetics of nitrate removal during UV-M/$S_2O_4{}^{2-}$ treatment of nitrate aqueous solutions (*lines* represent model predictions). Experimental conditions: *nitrate* 25 mg/L, *UV light intensity* 2,400 ± 10, room temperature (22–23 °C), natural pH (6.8)

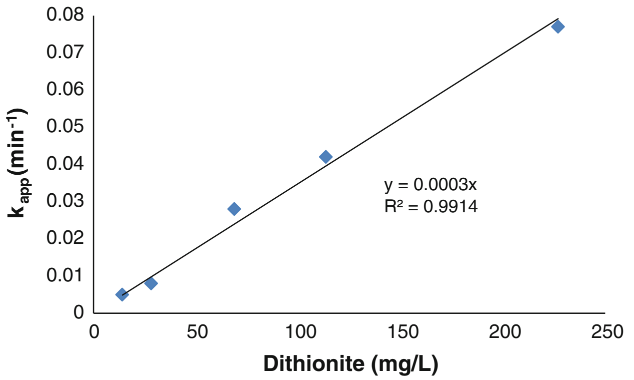

Fig. 5 Change of pseudo-first order kinetics with dithionite dose during UV-M/S2O42- treatment of nitrate aqueous solutions. Experimental conditions: *nitrate* 25 mg/L, *UV light intensity* 2,400 ± 10, room temperature (22–23 °C), natural pH (6.8)

- The increase in dithionite concentration enhances the production of $SO_2^{-\bullet}$ radical generated from the photodecomposition of dithionite ions with UV-M irradiation which leads to increasing the rate of nitrate reduction and improving the efficiency of UV-M/$S_2O_4^{2-}$ process.
- Increasing $S_2O_4^{2-}$ doses higher than 68.8 mg/L slightly increased the rate of nitrate reduction; however, similar efficiencies of UV-M/$S_2O_4^{2-}$ process are obtained for all $S_2O_4^{2-}$ doses toward the end of the experiment.
- If $S_2O_4^{2-}$ dose becomes higher than certain value, secondary reactions such as $SO_2^{-\bullet}$ radicals' recombination and dithionite disproportionation (reactions 9, 10, 11) (Kovacs and Rabai 2002; Read et al. 2001) will be accelerated and no significant production of $SO_2^{-\bullet}$ will be observed.

$$2SO_2^{-\cdot} \rightleftarrows S_2O_4^{2-} \tag{9}$$

$$2SO_2^{-\cdot} \rightleftarrows SO_2 + SO_2^{2-} \tag{10}$$

$$2\ S_2O_4^{2-} + H_2O \rightleftarrows 2SO_3^{2-} + S_2O_3^{2-} + 2H^+ \tag{11}$$

Therefore, no significant change in the rate of nitrate removal will be observed for high doses of $S_2O_4^{2-}$ above stoichiometric ratios.

Figure 6 shows the changes of nitrate concentration with time during UV-M/$S_2O_4^{2-}$ process treatment of aqueous solutions containing 25 mg/L nitrate with 68.8 mg/L dithionite at different initial pH values. It is markedly observed that no significant change in nitrate concentration was obtained at acidic conditions (pH 3.8). This could be due to the protonation of dithionite in acidic media. For neutral and alkaline pH conditions, almost total removal of nitrate was achieved after 240 min. However, decay of nitrate concentration under un-controlled pH (initial pH = 6.8) conditions was more rapid than that observed in phosphate-buffered solutions at pH 7 and 9.2. The results presented in Fig. 7 show minor effect of initial pH on nitrite formation/decay. For un-controlled pH conditions, formation and decay of nitrite ions was more rapid than that observed at neutral and alkaline buffered solutions. Furthermore, after 240-min treatment, nitrite was totally removed at un-controlled pH conditions; while small amounts of nitrite were detected at pH 7.0 and 9.2 buffered solutions. The experimental results of pH effects on nitrate removal by UV-M/$S_2O_4^{2-}$ process can be explained as follows:

- Under acidic conditions (pH < 4), fast auto-decomposition of dithionite ions occurs to form intermediates such as HSO_3^-, SO_3^{2-}, $S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_2O_5^{2-}$, which occurs in acidic pH (Danehy and Zubritsk 1974; Holman and Bennett 1994; DeCarvalho and Schwedt 2001). Decomposition of dithionite would reduce the production of $SO_2^{-\bullet}$, which would slow degradation of nitrate.
- At neutral and alkaline pH conditions, $S_2O_4^{2-}$ will be the dominant species, and it is easily activated by UV-M light and decomposes into $SO_2^{-\bullet}$ radicals that reduce nitrate efficiently.
- The fact that the rate of nitrate reduction in un-buffered is higher than the corresponding rate in phosphate-

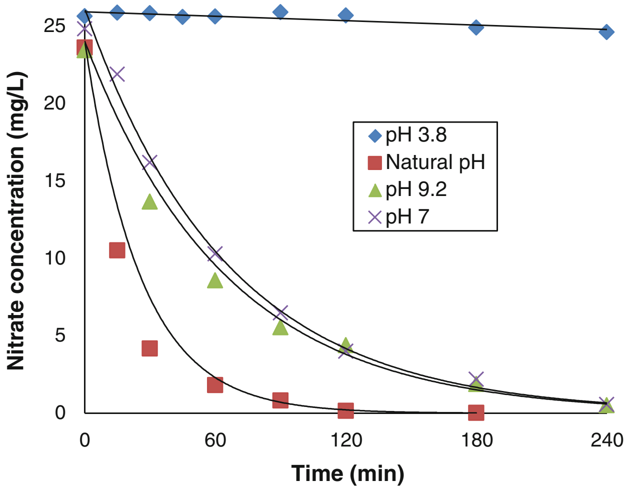

Fig. 6 Influence of initial pH on the kinetics of nitrate removal during UV-M/$S_2O_4^{2-}$ treatment of nitrate aqueous solutions. Experimental conditions: *nitrate* 25 mg/L, *dithionite* 68.8 mg/L, *UV light intensity* 2,400 ± 10, room temperature (22–23 °C), pH 3.8–9.2

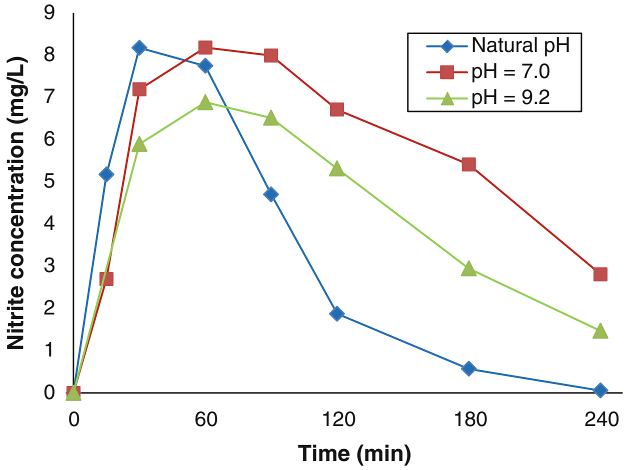

Fig. 7 Influence of initial pH on formation of nitrite during UV-M/$S_2O_4^{2-}$ treatment of nitrate aqueous solutions. Experimental conditions: nitrate: 25 mg/L, dithionite: 68.8 mg/L, UV light intensity: 2,400 ± 10, room temperature (22-23 °C), pH 3.8-9.2

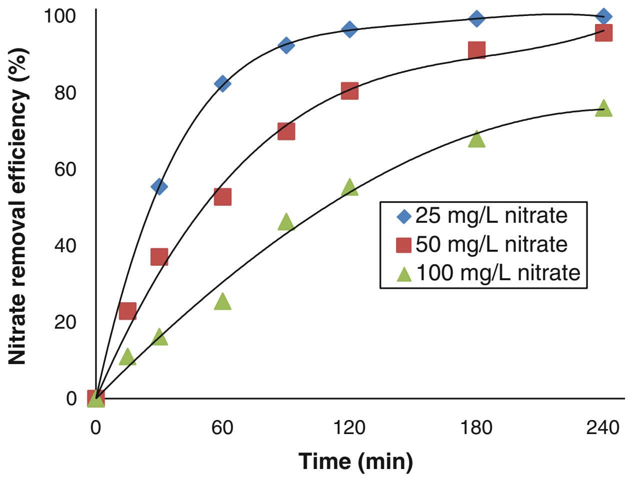

Fig. 8 Influence of nitrate concentration on nitrate removal during UV-M/$S_2O_4^{2-}$ treatment of nitrate aqueous solutions. Experimental conditions: *nitrate* 25–100 mg/L, [nitrate]/[dithionite] = 1, *UV light intensity* 2,400 ± 10, room temperature (22–23 °C), natural pH (6.8)

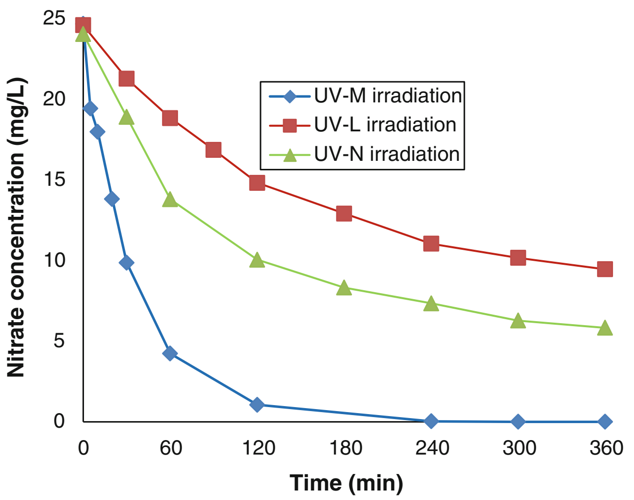

Fig. 10 Influence of UV light source on the kinetics of nitrate removal during UV-M/$S_2O_4^{2-}$ treatment of nitrate aqueous. Experimental conditions: *nitrate* 25 m/L, *dithionite* 68.8 mg/L, room temperature (22–23 °C), natural pH (6.8)

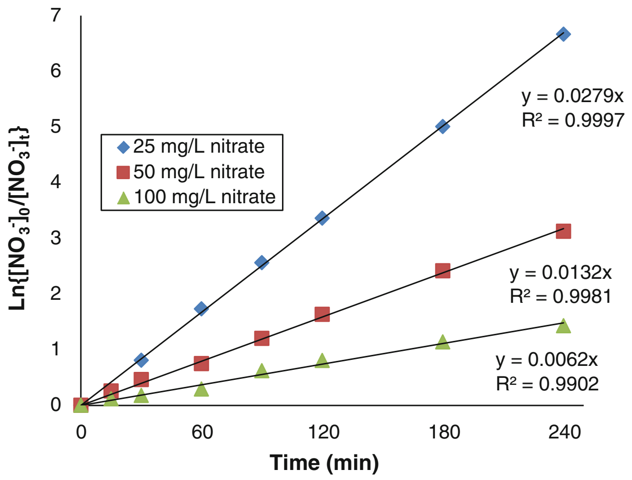

Fig. 9 Kinetics of nitrate removal during UV-M/$S_2O_4^{2-}$ treatment of aqueous solutions containing different nitrate concentrations (25, 50, 100 mg/L). Experimental conditions: *nitrate* 25–100 mg/L, [nitrate]/[Dithionite] = 1, *UV light intensity* 2,400 ± 10, room temperature (22–23 °C), natural pH (6.8)

buffered solutions could be due to the UV light absorbance by phosphate buffer and decrease in the available light that activates dithionite to produce the reactive radicals.

Figure 8 presents the influence of nitrate concentration on the rate and efficiency of nitrate removal by UV-M/$S_2O_4^{2-}$ process using stoichiometric amount of dithionite under natural pH. Removal efficiency of nitrate decreased with increasing initial nitrate concentration at the same ratio of dithionite dose to initial nitrate concentration. Removal efficiencies of nitrate were 99.9, 91.1, and 76.05 % after reaction time of 240 min at initial nitrate concentrations of 25, 50, and 100 mg/L, respectively. The rate of nitrate reduction also decreased with increasing initial nitrate concentration as shown in Fig. 9. Rate constants of 0.028, 0.0132, and 0.0062 $\min^{-1}$ were observed for initial nitrate concentrations of 25, 50, and 100 mg/L, respectively.

These results can be interpreted by the fact that the high concentrations of dithionite concentrations present at high initial nitrate concentrations resulted in decreasing the quantum yield of $S_2O_4^{2-}$-photodecomposition into $SO_2^{-\bullet}$ radicals. Increasing the lamp power might be required to achieve high nitrate removal efficiency when nitrate concentration in water is higher than 50 mg/L. The effect of lamp power was not part of this study. Moreover, high dithionite concentrations promote the consumption of $S_2O_4^{2-}$ by side reactions (Eqs. 9, 10, 11), and as a result, the efficiency of UV-M/$S_2O_4^{2-}$ process decreases. Additionally, high concentrations of nitrate and dithionite lead to the accumulation of nitrite ions which absorb more UV light and then decrease the quantum yield.

Figure 10 presents the effect of UV light type on the rate and efficiency of nitrate reduction with time during UV/$S_2O_4^{2-}$ treatment of aqueous solutions containing 25 mg/L nitrate with 68.8 mg/L dithionite and un-controlled pH. UV irradiation sources are low pressure (UV-L), medium pressure (UV-M), and narrow band (UV-N) UV lamps.

UV-L and UV-N lamps emit monochromatic UV light at 254 and 308 nm, respectively, while UV-M lamp emits polychromatic UV light in the range 200–600 nm. Only UV-M/$S_2O_4^{2-}$ combination achieved complete removal of nitrate. UV-N/$S_2O_4^{2-}$ combination was more efficient than UV-L/$S_2O_4^{2-}$. The observed difference of nitrate removal efficiency between UV-L and UV-N irradiation could be due to the fact that UV-N bulb produces almost all of its light at wavelengths near the maximum absorption of dithionite. Dithionite has an absorption peak in the ultraviolet near 315 nm. This wavelength is far from the wavelength that UV-L bulb emits and thus dithionite activation with UV-N to produce reducing radicals is more desirable than with UV-L. The highest efficiency of UV-M/$S_2O_4^{2-}$ process compared to UV-L and UV-N can be explained by the contribution of several routes in the mechanism of nitrate reduction. These engage the following: (1) direct photolysis of nitrate and its intermediates by UV-M irradiation, (2) chemical reduction of nitrate and its intermediates by dithionite and its by-products, (3) mediated reduction of nitrate and its intermediates by the free reducing radicals generated from photodecomposition of $S_2O_4^{2-}$.

Conclusion

The combination of UV irradiation using medium pressure lamp and dithionite (UV-M/$S_2O_4^{2-}$) was used to remove nitrate from water. This photochemical process produces sulfur dioxide reducing radical anions ($SO_2^{\bullet-}$) by symmetric dissociation of $S_2O_4^{2-}$. $SO_2^{\bullet-}$ species are instable and powerful reducing radicals capable of rapidly and efficiently reducing persistent oxidized species. UV-M/$S_2O_4^{2-}$ attained almost complete reduction of nitrate into ammonium and small amounts of volatile nitrogen species with formation of nitrite as intermediates. UV-M irradiation alone or chemical reduction with $S_2O_4^{2-}$ ions alone was not effective for nitrate removal. Nitrate reduction by UV-M/$S_2O_4^{2-}$ process follows pseudo-first-order kinetics. The apparent rate constant of nitrate reduction increases with increasing dithionite dose, but it decrease when nitrate concentration increases. UV-M/$S_2O_4^{2-}$ process can completely remove nitrate from water under neutral and alkaline conditions. However, it is ineffective in acid media ($pH < 4$). UV light source (UV-L, UV-M, or UV-N) has a significant influence on kinetics and efficiency of nitrate removal. Only UV-M/$S_2O_4^{2-}$ combination achieved total removal of nitrate. Also, UV-N/$S_2O_4^{2-}$ system was more efficient than UV-L/$S_2O_4^{2-}$.

Acknowledgments This publication was made possible by a grant from the Qatar National Research Fund under its National Priorities Research Program award number NPRP 4-1174-2-458. Its contents are solely the responsibility of the authors and do not necessarily represent the official views of the Qatar National Research Fund.

References

Barrabes N, Just J, Dafinov A, Medina F, Fierro JLG, Sueiras JE, Salagre P, Cesteros Y (2006) Catalytic reduction of nitrate on Pt–Cu and Pd–Cu on active carbon using continuous reactor-the effect of copper nanoparticles. Appl Catal B 62:77–85

Bludenko AV, Makarov IE, Ponomarev AV (2002) Effect of dissolved oxygen on the radiolytic conversion of nitrate ions in aqueous solutions in the presence of formate. Mendeleev Commun 12:164–165

Burow KR, Shelton JL, Dubrovsky NM (1998) Occurrence of nitrate and pesticides in ground water beneath three agricultural land-use settings in the eastern San Joaquin Valley, California, 1993–1995, water-resources investigations report 97-4284. US Geological Survey: Reston, VA. http://ca.water.usgs.gov/sanj/pub/usgs/wrir97-4284/wrir97-4284.html

Burow KR, Nolan BT, Rupert MG, Dubrovsky NM (2010) Nitrate in Groundwater of the United States, 1991–2003. Environ Sci Technol 44:4988–4997

Danehy JP, Zubritsk Cw (1974) Iodometric method for determination of dithionite, bisulfite, and thiosulfate in presence of each other and its use in following decomposition of aqueous-solutions of sodium dithionite. Anal Chem 46:391–395

DeCarvalho LM, Schwedt G (2001) Polarographic determination of dithionite and its decomposition products: kinetic aspects, stabilizers, and analytical application. Anal Chim Acta 436:293–300

Dell'Orco PC, Gloyna EF, Buelow SJ (1997) Reactions of nitrate salts with ammonia in supercritical water. Ind Eng Chem Res 36:2547–2551

Dence CW (1996) The chemistry of bleaching and brightness reversion. Chemistry of mechanical pulp bleaching. Pulp Bleach Princ Pract 1996:161–181

Drozdova Y, Steudel R, Hertwig RH, Koch W, Steiger T (1998) Structures and energies of various isomers of dithionous acid, $H_2S_2O_4$, and of its anion HS_2O_4-1. J Phys Chem A 102:990–996

Ellis ME (1996) The technology of mechanical pulp bleaching. Hydrosulfite (dithionite) bleaching. Pulp Bleach PrincPract 1996:491–512

Fan AM, Steinberg VE (1996) Health implications of nitrate and nitrite in drinking water: an update on methemoglobinemia occurrence and reproductive and developmental toxicity. Regul Toxicol Pharmacol 23:35–43

Fanning JC (2000) The chemical reduction of nitrate in aqueous solution. Coord Chem Rev 199:159–179

Fanning JC, Brooks BC, Hoeglund AB, Pelletier DA, Wadford JA (2000) The reduction of nitrate and nitrite ions in basic solution with sodium borohydride in the presence of copper(II) ions. Inorg Chim Acta 310:115–119

Gan H, Stucki JW, Bailey GW (1992) Reduction of structural iron in ferruginous smectite by free radicals. Clays Clay Miner 40:659–665

George M, Wiklund L, Aastrup M, Pousette J, Thunholm B, Saldeen T, Wernroth L, Zaren B, Holmberg L (2001) Incidence and geographical distribution of sudden infant death syndrome in relation to content of nitrate in drinking water and groundwater levels. Eur J Clin Investig 31:1083–1094

Ghafari S, Hasan M, Aroua MK (2008) Bio-electrochemical removal of nitrate from water and wastewater—a review. Bioresour Technol 99:3965–3974

Greer FR, Shannon M (2005) Infant methemoglobinemia: the role of dietary nitrate in food and water. Pediatrics 116:784–786

Gupta SK, Gupta AB, Gupta RC, Seth AK, Bassain JK, Gupta A (2000) Recurrent acute respiratory tract infections in areas with high nitrate concentrations in drinking water. Environ Health Perspect 108:363–365

Hodgson WG, Neaves A, Parker CA (1956) Detection of free radicals in sodium dithionite by paramagnetic resonance. Nature 178:489

Holman DA, Bennett DW (1994) A multicomponent kinetics study of the anaerobic decomposition of aqueous sodium dithionite. J Phys Chem 98:13300–13307

Huang YH, Zhang TC (2004) Effects of low pH on nitrate reduction by iron powder. Water Res 38:2631–2642

Huang CP, Wang HW, Chiu P-C (1998) Nitrate reduction by metallic iron. Water Res 32:2257–2264

Katsounaros I, Ipsakis D, Polatides C, Kyriacou G (2006) Efficient electrochemical reduction of nitrate to nitrogen on tin cathode at very high cathodic potentials. Electrochim Acta 52:1329–1338

Knobeloch L, Salna B, Hogan A, Postle J, Anderson H (2000) Blue babies and nitrate-contaminated well water. Environ Health Perspect 108:675–678

Kovacs KM, Rabai G (2002) Mechanism of the oscillatory decomposition of the dithionite ion in a flow reactor. Chem Commun 7:790–791

Kundu MC, Mandal B (2009) Nitrate enrichment in groundwater from long-term intensive agriculture: its mechanistic pathways and prediction through modeling. Environ Sci Technol 43:5837–5843

Li M, Feng C, Zhang Z, Yang S, Sugiura N (2010) Treatment of nitrate contaminated water using an electrochemical method. Bioresour Technol 101:6553–6557

Lindholm C-A (1999) Bleaching. Papermak Sci Technol 5:311–343

Liou YH, Lin CJ, Weng SC, Ou HH, Lo SL (2009) Selective decomposition of aqueous nitrate into nitrogen using iron deposited bimetals. Environ Sci Technol 43:2482–2488

Liu CS, Shih K, Wei L, Wang F, Li FB (2011) Kinetics and mechanism of propachlor reductive transformation through nucleophilic substitution by dithionite. Chemosphere 85:1438–1443

Ludwig RD, Su C, Lee TR, Wilkin RT, Ross RR, Keeley A (2007) In situ chemical reduction of Cr(VI) in groundwater using a combination of ferrous sulfate and sodium dithionite: a field investigation. Environ Sci Technol 41:5299–5305

Marchesini FA, Irusta S, Querini C, Miro E (2008) Nitrate hydrogenation over Pt, In/Al_2O_3 and Pt, In/SiO_2. Effect of aqueous media and catalyst surface properties upon the catalytic activity. Catal Commun 9:1021–1026

Murphy AP (1991) Chemical removal of nitrate from water. Nature 350:223–225

Nolan BT, Hitt KJ (2006) Vulnerability of shallow ground-water and drinking-water wells to nitrate in the United States. Environ Sci Technol 40:7834–7840

Ottley CJ, Davison W, Edmunds WM (1997) Chemical catalysis of nitrate reduction by iron (II). Geochimica Cosmochimica Acta 61:1819–1828

Pemberton RS, Depew MC, Heitner C, Wan JKS (1995) Some mechanistic insights into a model bleaching process for quinones by bisulfite and dithionite; an ESR–CIDEP study. J Wood Chem Technol 15:65–83

Pintar A, Batista J, Levec J (2001) Catalytic denitrification: direct and indirect removal of nitrates from potable water. Catal Today 66:503–510

Preston-Martin S, Pogoda JM, Mueller BA, Holly EA, Lijinsky W, Davis RL (1996) Maternal consumption of cured meats and vitamins in relation to pediatric brain tumors. Cancer Epidemiol Biomark Prev 5:599–605

Puckett LJ, Zamora C, Essaid H, Wilson JT, Johnson HM, Brayton M, Vogel JR (2008) Transport and fate of nitrate at the ground water/surface water interface. J Environ Qual 37:1034–1050

Read JF, John J, MacPherson J, Schaubel C, Theriault A (2001) The kinetics and mechanism of the oxidation of inorganic oxysulfur compounds by potassium ferrate. Part I. Sulfite, thiosulfate and dithionite ions. Inorg Chim Acta 315:96–106

Rinker RG, Gordon TP, Mason DM, Corcoran WH (1959) The presence of the $SO_2^{-\bullet}$ radical ion in aqueous solutions of sodium dithionite. J Phys Chem 63:302

Rivett MO, Buss SR, Morgan P, Smith JWN, Bemment CD (2008) Nitrate attenuation in groundwater: a review of biogeochemical controlling processes. Water Res 42:4215–4232

Rupert MG (2008) Decadal-scale changes of nitrate in ground water of the United States, 1988–2004. J Environ Qual 37: 240–248

Sanchez-Echaniz J, Benito-Fernandez J, Mintegui-Raso S (2001) Methemoglo-binemia and consumption of vegetables in infants. Pediatrics 107:1024–1028

Sato T, Sato K, Fujishiro Y, Yoshioka T, Okuwaki A (1996) Photochemical reduction of nitrate to ammonia using layered hydrous titanate/cadmium sulphide nanocomposites. J Chem Technol Biotechnol 67:345–349

Silva LA, Korn M, De-Andrade JB (2007) Influence of ultrasonic waves in the reduction of nitrate to nitrite by hydrazine–Cu(II). Ultrason Sonochem 14:275–280

Soares OSGP, Orfao JJM, Pereira MFR (2011) Nitrate reduction in water catalysed by Pd–Cu on different supports. Desalination 279:367–374

Szecsody JE, Fruchter JS, Williams MD, Vermeul VR, Sklarew D (2004) In situ chemical reduction of aquifer sediments: enhancement of reactive iron phases and TCE dechlorination. Environ Sci Technol 38:4656–4663

The Innovation Group (2008) Sodium hydrosulfite. http://www.the-innovation-group.com/ChemProfiles/Sodium%20Hydrosulfite.htm

Tsezou A, Kitsiou-Tzeli S, Galla A, Gourgiotis D, Papageorgious J, Mitrou S, Molybdas PA, Sinaniotis C (1996) High nitrate content in drinking water: cytogenetic effects in exposed children. Arch Environ Health 51:458–461

U.S. Environmental Protection Agency (2006) Ground water and drinking water. Consumer Factsheet on: Nitrates/Nitrites. http://www.epa.gov/safewater/dwh/c-ioc/nitrates.html

U.S. Environmental Protection Agency (2007) Nitrates summary. http://www.epa.gov/teach/chem_summ/Nitrates_summary.pdf

Volkmer BG, Ernst B, Simon J, Kuefer R, Bartsch G Jr, Bach D, Gschwend JE (2005) Influence of nitrate levels in drinking water on urological malignancies: a community-based cohort study. Br J Urol Int 95:972–976

Wasmuth CR, Edwards C, Hutcherson R (1964) Participation of the $SO_2^{-\bullet}$ radical ion in the reduction of p-nitrophenol by sodium dithionite. J Phys Chem 68:423–425

Yang GCC, Lee HL (2005) Chemical reduction of nitrate by nanosized iron: kinetics and Pathways. Water Res 39:884–894

Yang X, Yuan W, Gu S, Xiao F, Shen Q, Wu F (2007) $Na_2S_2O_4$ initiated free radical additions of polyfluoroalkyl halides to 4-pentenamides. J Fluorine Chem 128:540–544