

Article

UV sensitization of nitrate and sulfite: A powerful tool for groundwater remediation

Yaal Lester^{1,*}, Asmaa Dabash¹, Darine Eghbareya¹¹ Environmental Technologies, Department of Advanced Materials, Azrieli College of Engineering Jerusalem

* Corresponding author: email - yaalle@jce.ac.il; Tel.: +972-584-962214

Abstract:

Groundwater contamination by nitrate and organic chemicals (e.g. 1,4-dioxane) is a growing worldwide concern. This work presents a new approach for simultaneously treating nitrate and 1,4-dioxane, which is based on UV sensitization of nitrate and sulfite, and the production of reactive species. Specifically, water contaminated with nitrate and 1,4-dioxane is irradiated by a UV source (< 250 nm) at relatively high doses, to sensitize *in-situ* nitrate and generate HO•. This leads to the oxidation of 1,4-dioxane (and other organics), and the (undesired) production of nitrite as an intermediate. Subsequently, sulfite is added at an optimized time-point, and its UV sensitization produces hydrated electrons which reacts and reduces nitrite. Our results confirmed the effectivity of the proposed treatment: UV irradiation of nitrate (at > 5 mg N/L) efficiently degraded 1,4-dioxane, while producing nitrite at levels higher than 1 mg N/L (its MCL in drinking water). Adding sulfite to the process after 10 minutes of irradiation reduced the concentration of nitrite, without affecting the degradation rate of 1,4-dioxane. The treated water contained elevated levels of sulfate; albeit at much lower concentration than its MCL. Treating water contaminated with nitrate and organic chemicals (often detected concomitantly) typically requires several (expensive) treatment processes. The proposed approach may present a cost-effective alternative, employing a single system for the treatment of nitrate and organic contaminants.

Keywords: Photo-sensitization; nitrate; sulfite, 1,4-dioxane, groundwater

1. Introduction

Dissolved water constituents can act as photosensitizers, which absorb light and produce reactive species such as hydroxyl radical (HO•). These photo-generated reactive species may further react and degrade organic water contaminants. Photosensitizers can be employed for water treatment, as in the case of some advanced oxidation processes (AOPs), which combine UV irradiation with hydrogen peroxide or semiconductors. Alternatively, photosensitizers such as iron, nitrate, and dissolved organic matter can be found in natural systems; where their solar light photo-generated radicals degrade organic pollutants and affect their lifetime in aquatic environments [1–3].

This study focuses on two photosensitizers, nitrate (NO₃⁻) and sulfite (SO₃²⁻), and their application for groundwater treatment. The mechanism of nitrate sensitization was already identified in the late 60s [4,5]. Nitrate irradiation with UV light (at wavelengths < 240 nm and 300 - 325 nm) generates OH• radicals, nitrite ions (NO₂⁻) (which may further photo-generate OH•), as well as other products such as peroxynitrite [6]. Irradiation of sulfite with UV light (< 250 nm), on the other hand, generates reducing radicals such as hydrated electrons (e_{aq}⁻) and sulfite radical anions (SO₃^{•-}), in a process commonly known as advanced reduction [7].

Despite the long-recognized mechanism of OH• generation by photo-sensitized nitrate, only recently researchers have suggested that this process can be employed for wastewater treatment. Keen et al. [8] showed that irradiation of nitrate (> 5 mg N/L) with medium pressure (MP) mercury lamp generates similar OH• concentration as irradiating 10 mg/L H₂O₂ (the well-known UV/H₂O₂ process); thus, the combination MP UV/NO₃ is a *de facto* AOP. These results were later-on confirmed

by Lester et al. [9], which showed that the degradation rate of different organic contaminants by UV/H₂O₂ (low-pressure UV lamp, 10 mg/L H₂O₂) was comparable to their degradation by UV/NO₃ (MP UV lamp, indigenous nitrate 14 mg N/L), using a pilot wastewater treatment system.

Applying UV/NO₃ for groundwater treatment may be highly advantageous, due to the potential use of naturally-occurring nitrate. Nitrate is frequently detected in groundwater aquifers around the world [10–12], mainly as a result of intense agricultural activity. In the U.S., for example, the Geological Survey National Water-Quality Assessment (NAWQA) program has found nitrate at concentration higher than 1 mg N/L in 50% of groundwater wells (supplying drinking water) throughout the country [13], with higher concentrations detected in rural areas. In Israel, average nitrate concentration in the coastal aquifer (Israel's most densely populated area) was 13.3 mg N/L on 2000 [11].

Another class of important groundwater contaminants (often detected in concomitant with nitrate) are organic chemicals, such as pesticides, chlorinated solvents and 1,4-dioxane [14–16]. These chemicals are often carcinogens, and their removal from groundwater is highly challenging (The Israel Water Authority, 2017). In this context, (conventional) AOPs were able to efficiently degrade many of these organic contaminants, due to the fast reaction of OH• with most compounds [17–19]. However, AOPs are often limited by their high operational cost [e.g. the cost of hydrogen peroxide; ,20]. Therefore, using *in-situ* nitrate to generate OH• and degrade industrial (and other) organic groundwater contaminants, may present an attractive cost-effective alternative for conventional AOPs.

One of the main concerns regarding UV irradiating of nitrate is the photo-generation of nitrite as a byproduct (a harmful contaminant with lower Maximum Contaminant Level - MCL than nitrate). Although former studies showed that nitrite level will remain well below its MCL during typical MP UV disinfection of nitrate-containing water [21], employing UV for oxidation of organic constituents—which requires much higher UV doses—may result in elevated concentrations of nitrite. To control excess nitrite, we employed a relatively new, underexplored approach: the use of reducing radicals, which degrade nitrite to harmless products. These radicals were produced by introducing sulfite into the UV treatment (UV/SO₃) at a specific time-point. UV/SO₃ previously showed effective reduction of different oxidized inorganic compounds, including perchlorate, bromate and even nitrate [22–24].

The goals of this study were to (i) evaluate the feasibility of MP UV/NO₃ at high UV doses for the degradation of 1,4-dioxane, while monitoring the concentrations of nitrate and nitrite and (ii) propose a new sequential groundwater treatment process: UV sensitization of *in-situ* nitrate (to oxidize 1,4-dioxane and other organics) followed by UV sensitization of (added) sulfite (to reduce photo-generated nitrite). This process showed high potential in degrading both nitrate and 1,4-dioxane, while keeping nitrite at low concentrations.

2. Materials and Methods

2.1. Reagents and Chemicals

Analytical grade (>98%) 1,4-dioxane, sodium nitrate, sodium nitrite, and sodium sulfite were obtained from Sigma-Aldrich. Deionized water (resistance = 18.2 MΩ·cm) was obtained from a Millipore Milli-Q purification system. All chemicals were used as received. Initial 1,4-dioxane concentration during experiments was 10 μM (unless mentioned otherwise).

2.2. Experimental Setup

Irradiation was performed in a temperature controlled (25°C) 2.5 L glass cylindrical batch reactor. The center of the reactor was occupied with a quartz sleeve in which a 0.45 kW MP UV lamp was placed vertically (Ace-Hanovia). Average fluence-rate inside the reactor was approximately 9 mW/cm², measured using nitrate actinometry developed by Goldstein & Rabani [25].

2.3. Analytical Methods

1,4-Dioxane was measured using HPLC (Agilent 1100 series; Synergi 4 μm Fusion - RP column 2 mm \times 250 mm) coupled with a mass spectrometer (Q-TOF MS, Waters Premier). The mobile phase consisted of water with 10% acetonitrile. Nitrate and nitrite were quantified by ECO Ion Chromatograph (Metrohm, Switzerland). Ammonia was measured using HACH salicylate method.

3. Results and Discussion

3.1. UV/NO₃ degradation of 1,4-dioxane: The impact of initial nitrate concentration

Degradation of 1,4-dioxane by UV/NO₃ is presented in Figure 1, for nitrate concentrations 0 (UV alone) and 5 mg N/L (in buffered deionized water at pH 7.8). Direct photolysis of 1,4-dioxane was relatively slow, due to the compound's extremely low UV light absorption [17]. Adding 5 mg N/L nitrate, on the other hand, enhanced the degradation of the contaminant, most likely as a result of its reaction with photo-generated OH \bullet . This assumption was backed-up by the impact of initial nitrate concentration on 1,4-dioxane degradation rate (inset of Figure 1); where, further increasing nitrate concentration up to 16 mg N/L (~70 mg/L nitrate; the Israeli MCL in drinking water; <https://www.health.gov.il/English>) did not result in higher degradation rate. This trend is typical for nitrate-generated OH \bullet reactions [8], which can be explained by the fast reaction of OH \bullet with photo-generated nitrite [$k_{\text{OH}\bullet,\text{NO}_2}$ 1×10^{10} 1/Ms; ,26], inhibiting the rate 1,4-dioxane degradation at high concentration of nitrate:

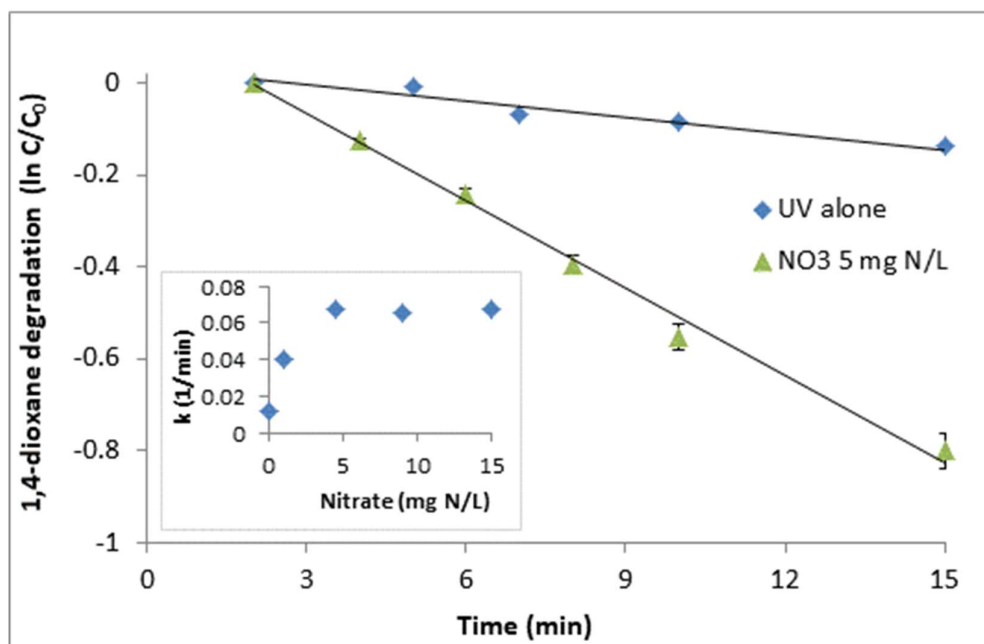
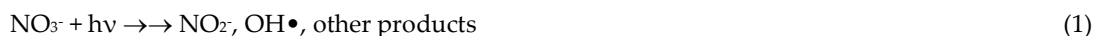


Figure 1. Degradation of 1,4-dioxane by UV alone and by UV/NO₃ (5 mg N/L). The inset presents the first-order rate constants vs. initial nitrate concentration. Experiments conducted in buffered DI at pH 7.8

3.2. Nitrate decay and nitrite formation

Nitrite is by far the most important byproduct of nitrate photolysis [6], especially at high UV doses. Figure 2 illustrates nitrate decay and nitrite formation during UV/NO₃⁻, for different initial nitrate concentrations.

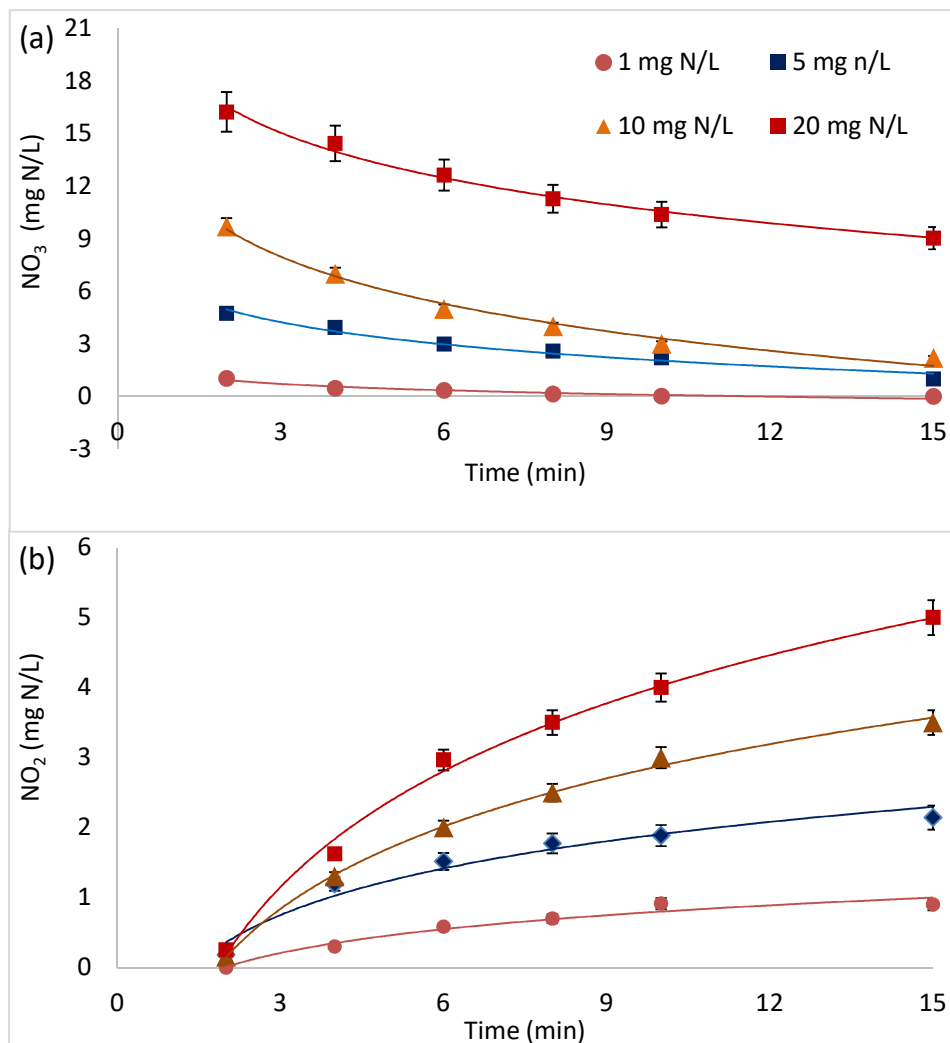


Figure 2. Nitrate decay (a) and nitrite formation (b) at different initial NO₃⁻ concentrations

Nitrate concentration decreased significantly with irradiation, in parallel to the formation (and accumulation) of nitrite. Concentration of nitrite quickly reached (and in most cases overpassed) the U.S. EPA drinking water standard of 1 mg N/L, even at the lowest initial nitrate concentration. Previous studies found much lower nitrite concentrations during UV/NO₃⁻; however, these studies applied UV doses up to 400 mJ/cm² [21] and 700 mJ/cm² [27]. For comparison, UV dose in our study was evaluated as approximately 3000 mJ/cm² at 6 min irradiation (calculated as the product of measured fluence-rate and irradiation time). Based on our results, it is clear that at high UV doses, nitrite formation is significant and cannot be overlooked.

3.3. Effect of bicarbonate on the UV/NO₃⁻ process

Carbonate species are ubiquitous in groundwater, and are important factors in the efficiency of AOPs (due to their fast reaction with OH•). We examined the impact of bicarbonate on UV/NO₃⁻ in the range of 0 – 300 mg/L, typical for Israel's groundwater (Israel Water Authority;

<http://www.water.gov.il/>). Increasing the concentration of bicarbonate up to 200 mg/L only marginally affected 1,4-dioxane degradation (Figure 3); however, at higher concentrations (300 mg/L) bicarbonate reduced the degradation rate of 1,4-dioxane by approximately 25%. Carbonates concentration of 300 mg/L was determined by the US Army Corps of Engineers as the threshold for water treated by UV-AOP (<https://standards.globalspec.com/std/499272/coe-etl-1110-1-161>). Higher carbonates levels were found to have a terminal effect on the process due to $\text{OH}\cdot$ scavenging.

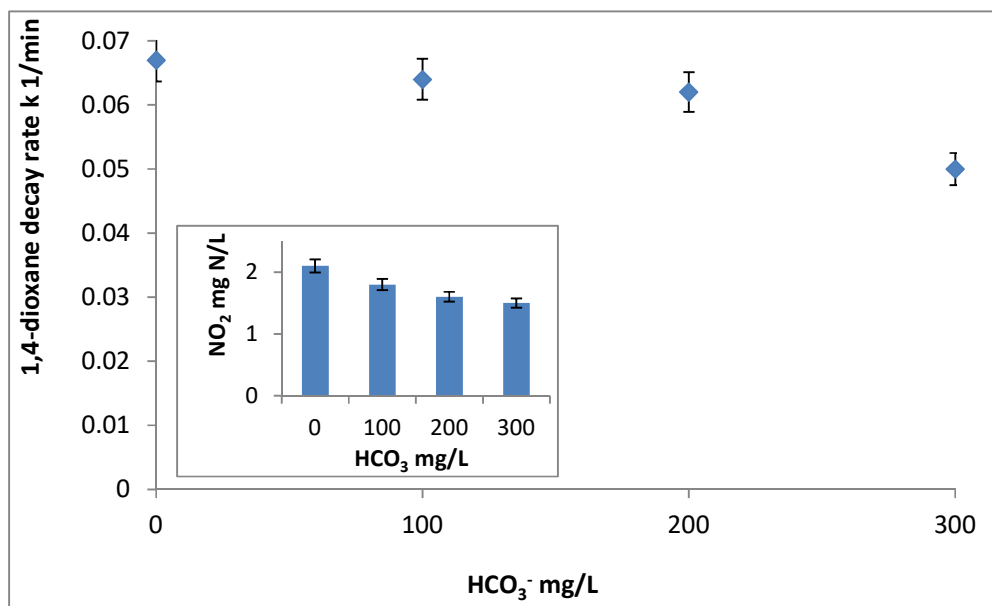


Figure 3. Rate constant of 1,4-dioxane degradation by UV/NO₃ (5 mg N/L), at different bicarbonate concentrations. The inset show produced nitrite concentrations in presence of bicarbonate after 15 min of UV irradiation of nitrate (5mg N/L) and 1,4 dioxane (10 μM) containing solution

Additionally, increasing bicarbonate concentration lowered nitrite formation rate, as illustrated in the inset of Figure 3. Similar phenomenon was observed by Sharpless and Linden [21], where, the yield of nitrite formation during UV/NO₃ was significantly decreased with the addition of bicarbonate (at pH 8). The researchers explained this trend by reaction of CO₂(aq) with peroxyxynitrite (an intermediate in nitrite formation), preventing its transformation into nitrite. It should be noted however, that even at the highest bicarbonate concentration examined, nitrite level was reduced by no more than 25%, and was still significantly above 1 mg N/L.

3.4. Nitrite reduction by UV/SO₃

Controlling the level of nitrite during UV/NO₃ is imperative for any future application of the proposed process. In our case, nitrite concentration was reduced by the addition of sulfite to the UV/NO₃ process, after 10 minutes of irradiation, to produce reducing radicals which further degrade nitrite. Preliminary experiments were conducted to determine (i) the impact of sulfite on nitrite concentration (without UV) and (ii) the effect of sulfite addition at the beginning of irradiation. The former experiment showed that sulfite alone could not reduce nitrite; whereas the latter resulted in slower degradation of 1,4-dioxane (than sulfite addition after 10 minutes). Sulfite largely absorb light at < 250 nm; thus its addition at the beginning of irradiation reduces the amount of light absorbed by nitrate, leading to lower $\text{OH}\cdot$ production and slower 1,4-dioxane degradation.

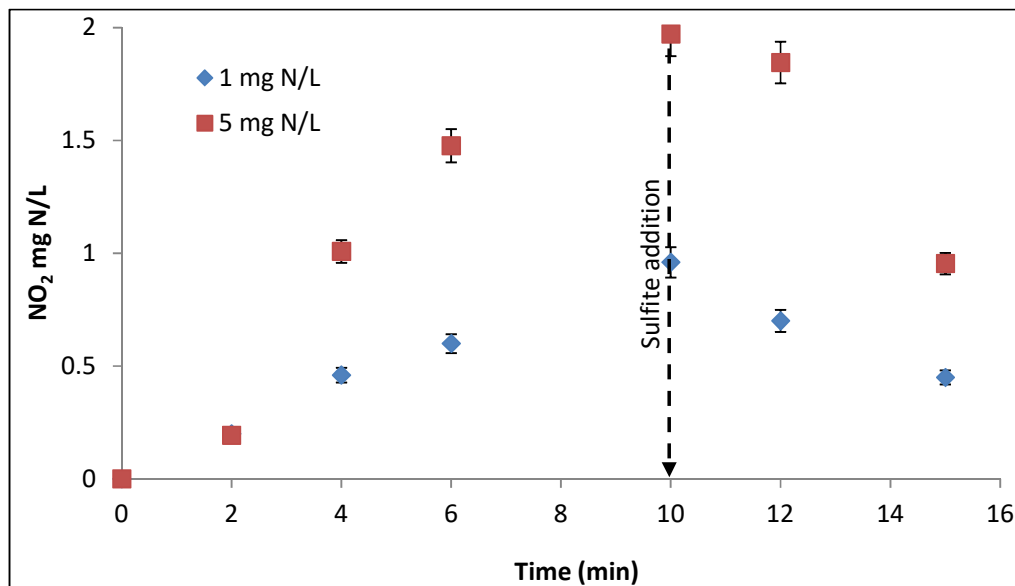


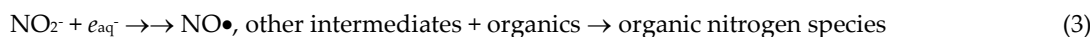
Figure 4. Nitrite concentration during UV/NO₃ (at initial NO₃⁻ concentrations 1 and 5 mg N/L). Sodium sulfite was added at 10 min, at concentrations 50 and 100 mg/L for the low and high NO₃⁻ concentrations respectively. 1,4-dioxane was at 10 μM.

Figure 4 illustrates the effect of sulfite addition on the concentration of nitrite during UV/NO₃ for initial nitrate levels of 1 and 5 mg N/L (sulfite was added at 50 and 100 mg/L, respectively). Nitrite concentration dropped by approximately 50% after five minutes from addition of sulfite, most likely due to its reaction with the photo-sensitized reducing radicals. Degradation of 1,4-dioxane was only marginally affected by sulfite addition (results not shown). Early studies showed that nitrite quickly reacts with e_{aq}^- ($k = 4.1 \times 10^9$ 1/Ms, [26]), producing nitric oxide (NO•) and other intermediates [28]. Sulfite radicals were oxidized into (harmless) sulfate (SO₄²⁻) [7], as implied by the increase in sulfate concentration with time (Table 1).

Table 1. Concentrations of sulfite and sulfate at 12 and 15 minutes of irradiation

Initial NO ₃	Sulfite (mg/L)		Sulfate (mg/L)	
	12 min	15 min	12 min	15 min
1 mg N/L	35 (±4)	12 (±2)	11 (±3)	23 (±4)
5 mg N/L	61 (±7)	42 (±5)	15 (±2)	28 (±5)

Nitrite reduction by e_{aq}^- can proceed via several pathways, each generating different stable end products [28–30]:



To elucidate the dominant mechanism, we conducted a UV/NO₃ + SO₃²⁻ experiment (initial NO₃⁻ concentrations 1 mg N/L) in organic-free water (i.e., without 1,4-dioxane addition), while monitoring nitrite, nitrate, and ammonia. Concentrations of nitrate and nitrite followed the trends observed earlier; nitrate concentration steadily decreased while nitrite concentration increased at first, then decreased following SO₃²⁻ addition. Ammonia concentration remained below detection limit (< 0.1

mg N/L) in all measured samples. Based on these results, we suggest that the main product of nitrite reduction by e_{aq}^- is nitrogen gas. It should be noted however, that when organic matter is present, production of organic nitrogen species might occur.

3.5. Implications for groundwater remediation

Nitrate (NO_3^-) and 1,4-dioxane are two of the most important groundwater contaminants in Israel (and worldwide), responsible for most disqualifications of groundwater wells in the coastal aquifer of the country (Israel Water Authority). While treating nitrate contamination is feasible but costly (usually through ion exchange or biological processes), removing 1,4-dioxane from groundwater is much more challenging. 1,4-dioxane is non-biodegradable and cannot be removed by sorption or air-stripping, due to its high solubility and low vapor pressure [17]. Moreover, 1,4-dioxane is poorly removed during reverse osmosis desalination [31], and conventional AOPs (e.g. UV/ H_2O_2) are typically too costly to be applied at large scale [20].

Here, we demonstrated a (potentially cost-effective) treatment process, which is able to simultaneously remove nitrate and 1,4-dioxane from groundwater. Our results imply that MP UV irradiation (at relatively high doses), with addition of sulfite at an optimized time-point, has the potential to degrade nitrate and 1,4-dioxane (and possibly other organic contaminants), while keeping nitrite level below its MCL. The produced water is expected to have elevated concentrations of sulfate; however, this ion is relatively harmless with mostly organoleptic effect (MCL of 250 mg/L; Israel Ministry of Health). A schematic representation of the proposed treatment is illustrated below.

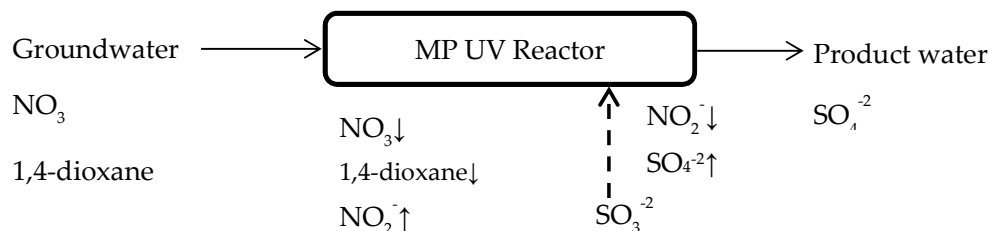


Figure 5. Schematic representation of the UV/ $\text{NO}_3^- + \text{SO}_3^{2-}$ treatment

In evaluating the applicability of the proposed process, some additional points should be kept in mind: (i) the process is only valid for groundwater containing both organic contaminants and nitrate (preferably at > 5 mg N/L), (ii) extended work should be conducted, mainly with regard to optimization sulfite concentration and injection point and (iii) the impact of other water constituents should be evaluated. For example, nitrate photolysis in the presence of aromatic compounds may produce potent nitroaromatics [32]. While these compounds will likely be degraded at the high UV doses applied (> 3000 mJ/cm²), their potential formation should not be overlooked.

Author Contributions: conceptualization, Yaal Lester; methodology, Yaal Lester; formal analysis, Yaal Lester; investigation, Asmaa Dabash and Darine Eghbareya; writing—original draft preparation, Yaal Lester.

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

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