


Article

Interconversion and Removal of Inorganic Nitrogen Compounds via UV Irradiation

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Abstract: Dissolved inorganic nitrogen (DIN) species are key components of the nitrogen cycle and are the main nitrogen pollutants in groundwater. This study investigated the interconversion and removal of the principal DIN compounds (NO_3^- , NO_2^- and NH_4^+) via UV light irradiation using a medium-pressure mercury lamp. The experiments were carried out systematically at relatively low nitrogen concentrations (1.5 mM) at varying pHs in the presence and absence of oxygen to compare the reaction rates and suggest the reaction mechanisms. NO_3^- was fully converted into NO_2^- at a pH > 3 in both oxic and anoxic conditions, and the reaction was faster when the pH was increased following a first-order kinetic at pH 11 ($k = 0.12 \text{ min}^{-1}$, $R^2 = 0.9995$). NO_2^- was partially converted into NO_3^- only at pH 3 and in the presence of oxygen and was stable at an alkaline pH. This interconversion of NO_3^- and NO_2^- did not yield nitrogen loss in the solution. The addition of formic acid as an electron donor led to the reduction of NO_3^- to NH_4^+ . Conversely, NH_4^+ was converted into NO_2^- , NO_3^- and to an unidentified subproduct in the presence of O_2 at pH 10. Finally, it was demonstrated that NO_2^- and NH_4^+ react via UV irradiation with stoichiometry 1:1 at pH 10 with the total loss of nitrogen in the solution. With these results, a strategy to remove DIN compounds via UV irradiation was proposed with the eventual use of solar light.

Keywords: nitrogen removal; inorganic nitrogen; photolysis; reactive nitrogen species



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1. Introduction

The chemical element nitrogen (N) is a key component of life. Its most abundant form on Earth is atmospheric dinitrogen (N_2). However, N_2 is unavailable for most organisms, making N a limiting nutrient. Therefore, N compounds in nature can be classified into two groups: nonreactive N (N_2) and reactive N (N_r). N_r includes all biologically, photochemically, and radiatively active N compounds in the Earth's atmosphere and biosphere [1]. N_r can be found in both organic and inorganic compounds. Organic compounds include urea, amines, proteins, and nucleic acids. Inorganic compounds can be gaseous (e.g., nitrous oxide (N_2O), nitrogen oxide (NO) and nitrogen dioxide (NO_2), with the last two known as NO_x) and also can be present in soil and water. The most common dissolved inorganic nitrogen (DIN) compounds in water are nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+). In particular, NO_3^- is the main nitrogen groundwater pollutant [2].

In the natural cycle of N, N_2 is converted into N_r by lightning and by biological nitrogen fixation. The reverse reaction in the cycle converts organic N and NH_4^+ into NO_2^- and NO_3^- (nitrification) and then to N_2 (denitrification). A few decades ago, these opposite processes were approximately equal. However, in recent times, anthropogenic activity [3] has led to an imbalance between these processes, resulting in the accumulation of N_r in the environment. This includes the industrial Haber–Bosch process that converts N_2 into NH_3 used in the synthesis of fertilizers for food production and the fossil-fuel

combustion that converts fossil N into NO_x [4]. To overcome the N_r accumulation, the natural nitrification/denitrification process has been implemented in wastewater treatment plants [5]. Recently, another biological process, autotrophic anaerobic ammonium oxidation (Anammox), has been used on a large scale [6]. In this process, NH_4^+ is oxidized with NO_2^- to yield N_2 via a biologically mediated process. DINs can also be removed using traditional physicochemical treatments, such as ion exchange, adsorption, etc. [7].

Therefore, DINs are key compounds in the nitrogen cycle and water treatment technologies. In particular, the photocatalytic reduction of NO_3^- into N_2 is emerging as an alternative to the removal of nitrogen from water [7]. TiO_2 is the most studied photocatalyst for this purpose but the interconversion of inorganic nitrogen compounds can also be achieved without it via simple UV irradiation [8]. The absorption spectra of NO_3^- and NO_2^- are dominated by intense $\pi \rightarrow \pi^*$ bands at 200 nm ($\epsilon = 9900 \text{ M}^{-1} \text{ cm}^{-1}$) and 205 nm ($\epsilon = 5500 \text{ M}^{-1} \text{ cm}^{-1}$), respectively. But they also present weaker $n \rightarrow \pi^*$ bands at 310 nm ($\epsilon = 7.4 \text{ M}^{-1} \text{ cm}^{-1}$) and 360 nm ($\epsilon = 22.5 \text{ M}^{-1} \text{ cm}^{-1}$), respectively. These last bands can absorb solar radiation ($\lambda > 295 \text{ nm}$), and they are important not only for solar-based technologies but also for processes initiated by sunlight in natural waters and in atmospheric aerosols [9]. Brown carbon aerosols are light-absorbing particles primarily originating from biomass combustion. Comprising near-UV-absorbing organic compounds mixed with NO_3^- within atmospheric aerosols, these aerosols are thought to contribute to the presence of nitrous acid in the atmosphere through the photolysis of NO_3^- into NO_2 and NO_2^- [10].

Although NH_4^+ does not absorb significantly within the UV-vis spectra, it can be oxidized through photocatalytic methods [11]. The removal of $\text{NH}_4^+/\text{NH}_3$ via oxidation poses a significant challenge due to its high stability and water solubility. Photocatalytic oxidation using TiO_2 (P25), particularly at high pH conditions, has been successful at converting $\text{NH}_4^+/\text{NH}_3$ into N_2 [12]. In this investigation, we explored $\text{NH}_4^+/\text{NH}_3$ oxidation via irradiation in the presence of oxygen, omitting the use of a catalyst.

Usually, irradiation experiments have been undertaken to study DIN species separately. This work attempts to describe systematically the main features arising from the irradiation of DIN species by applying similar conditions but also through the simultaneous irradiation of NO_2^- and NH_4^+ . In this specific scenario, prior research [13] demonstrates that photolysis exhibits superior performance compared to the photocatalytic process for nitrogen removal. The focus was placed on the main DIN compounds (NO_3^- , NO_2^- and NH_4^+) in a relatively low total nitrogen concentration (1.5 mM).

The irradiation of DINs produces nitrogen radicals and OH^\bullet , which subsequently facilitates the oxidation of organic matter. This approach has garnered attention for its potential in addressing environmental challenges, particularly in the oxidation of emerging contaminants of concern (CECs) through UV irradiation when residual NO_2^- is present [14]. In this study, formic acid (HCOOH) was selected as the target organic compound for oxidation due to its convenient mineralization and traceable degradation process.

The irradiation was aimed to excite the $n \rightarrow \pi^*$ absorption bands of the compounds, which have implications in solar applications. For this purpose, a medium-pressure mercury lamp (main emission bands between 313 and 436 nm) was used in contrast with other studies that employ low-pressure mercury lamps (maximum emission at 254 nm) that excite the $\pi \rightarrow \pi^*$ bands principally [15]. A discussion was completed about the interconversion of DINs, the possible intermediates and the potential conversion into N_2 for the nitrogen removal from water.

2. Materials and Methods

2.1. Chemicals

Solutions were prepared with KNO_3 (>99%, Mallinkrodt), NaNO_2 (>99%, Merck), NH_4OH (30%, Anedra) and HCOOH (88%, Biopack) and used without further purification. For pH adjustments, H_2SO_4 (Biopack) or NaOH (Biopack) was used. Analytical calibration standards of KNO_3 , NaNO_2 and NH_4Cl were obtained from ChemLab. All experiments

were performed with MilliQ water (resistivity = 18 M Ω cm), and all mentioned chemicals were analytical grade or superior.

2.2. Irradiation Experiments

Irradiation experiments were performed in an immersion well reactor (Figure 1) consisting of a thermostatted (298 K) annular reactor (130 mm length, 57 mm external diameter, 48 mm internal diameter, 160 mL total cell volume). The irradiation source was a medium-pressure mercury lamp installed inside the reactor (Photochemical Reactors Ltd., Reading, UK). This lamp emits radiation between 300 and 440 nm with main peaks at 313, 366, 404 and 436 nm (Figure S1 in Supplementary Material includes the emission spectrum of the medium-pressure Hg lamp together with the absorption bands of NO₃⁻ and NO₂⁻). Actinometric measurements were performed using the ferrioxalate method. An incident photon flux per unit volume (q_p/V , where q_p is the incident photon flux, and V is the irradiated volume) of 3.2×10^{-4} $\mu\text{einstein s}^{-1} \text{L}^{-1}$ was calculated. In all cases, 200 mL of NO₃⁻ (1.5 mM), NO₂⁻ (1.5 mM), NH₃/NH₄⁺ (1.5 mM), NO₂⁻ (0.75 mM) + NH₃/NH₄⁺ (0.75 mM) or NO₃⁻ (1.2 mM) + HCOOH (30 mM) solutions was adjusted to the desired pH using dropwise addition of H₂SO₄ (0.5 M) or NaOH (0.5 M) into the reservoir where argon or oxygen (0.2 L min⁻¹) was constantly bubbled. All the experiments were performed at 25.0 ± 0.1 °C. Solutions in the reservoir were magnetically stirred throughout the reaction time. Samples (1 mL) were periodically extracted for analysis, and the pH was measured. All runs were performed at least in duplicate, and the results were averaged. The experimental error was never higher than 10%.

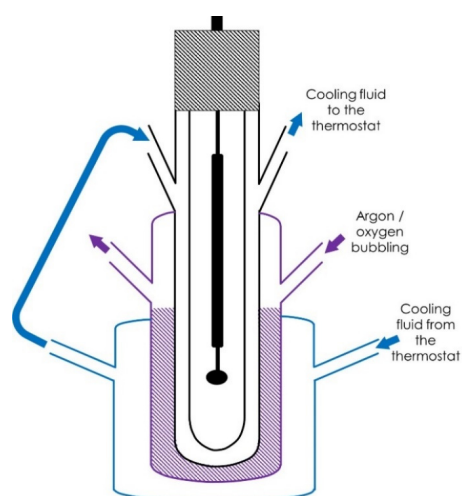


Figure 1. Scheme of the irradiation setup.

2.3. Analytical Techniques

Periodically withdrawn samples were conditioned to determine [NO₃⁻], [NO₂⁻], [NH₄⁺] and [HCOOH]. The concentrations of NO₃⁻, NO₂⁻ and NH₄⁺ were measured spectrophotometrically using the standard methods SM-4500-NO₃-E [16], SM-4500-NO₂-B [17] and SM-4500-NH₃-F [18], respectively, employing an HP8453A spectrophotometer (Hewlett-Packard) with UV detection. HCOOH concentration was determined using a Shimadzu 5000 A TOC analyzer in the non-purgeable organic carbon (NPOC) mode.

3. Results and Discussion

3.1. Irradiation of NO₃⁻

Figure 2 shows the removal of aqueous NO₃⁻ (dashed lines) and the parallel NO₂⁻ formation (solid lines) due to the irradiation of the nitrate solutions in a pH range from 3 to 11 with a medium-pressure mercury lamp in anoxic conditions. The reaction rate

increased when varying from an acid to alkaline solution, yielding NO_2^- as the main product (Equation (1)).

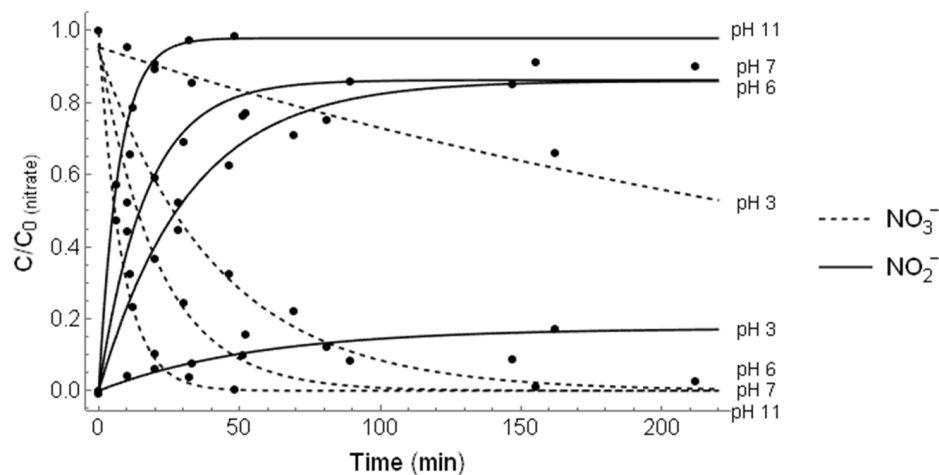


Figure 2. NO_3^- (dashed lines) and NO_2^- profiles (solid lines) vs. time obtained after the irradiation of NO_3^- (1.5 mM) at varying pH conditions. The solutions were continuously purged with argon.

At a neutral and acidic pH, the nitrogen mass balance of NO_3^- , NO_2^- and NH_4^+ in the solution during irradiation indicates that they did not account for 100% of the nitrogen introduced in the system as NO_3^- . This discrepancy is likely attributed to a loss of nitrogen from the aqueous phase. As presented in Table 1, the nitrogen recovery considers the total nitrogen found in the solution after the reaction (i.e., nitrogen originating from NO_3^- , NO_2^- and NH_4^+). The observed behavior concerning the influence of the solution pH is consistent with findings reported by other authors who have utilized a low-pressure mercury lamp [15].

Table 1. Kinetics of the photo reduction of NO_3^- at varying pH conditions. The data presented were calculated by performing a mathematical adjustment of the kinetic curves presented in Figure 2. Nitrogen recovery was calculated as $100 \times ([\text{NO}_3^-]_f + [\text{NO}_2^-]_f + [\text{NH}_3]_f) / [\text{NO}_3^-]_i$.

Purge	pH	Kinetic Rate Constant (min^{-1})	Correlation Coefficient (R^2)	Nitrogen Recovery (%)
Argon	3	0.003	0.9980	83
	6	0.024	0.9917	93
	7	0.048	0.9879	92
	11	0.121	0.9995	99
Oxygen	10	0.084	0.9919	92

The total reduction of NO_3^- to NO_2^- was also confirmed in oxic conditions at an alkaline pH (Table 1), indicating that the presence of oxygen in the system did not affect the reduction of NO_3^- .

The observed pH dependence could be explained by the formation of peroxyntrous acid (ONOOH)/peroxynitrite (ONOO^-) species considered to be one of the main intermediates of the photo reduction of NO_3^- [7]. ONOOH is unstable, and it isomerizes to NO_3^- (Equation (2)), thereby reversing the reaction (1) [19]. This acid has a $\text{pK}_a = 6.5$; therefore, at pH higher than 6.5, ONOO^- predominates, and the reaction continues to yield NO_2^- without reversing to NO_3^- .



3.2. Irradiation of NO_2^-

The oxidation of NO_2^- into NO_3^- through irradiation was partially achieved at pH 3 in the presence of O_2 . In these conditions, 30% of NO_2^- (1.5 mM) was converted into NO_3^- within 2 h (Figure 3). Initially, when the NO_2^- solutions were prepared at pH 3, a rapid dark reaction leading to the oxidation of NO_2^- into NO_3^- was observed. Therefore, experiments at this pH were initiated with the presence of NO_3^- , as shown in Figure 3. In contrast, at a higher pH or in the absence of O_2 , this reaction was not significant, indicating the stability of NO_2^- in the dark.

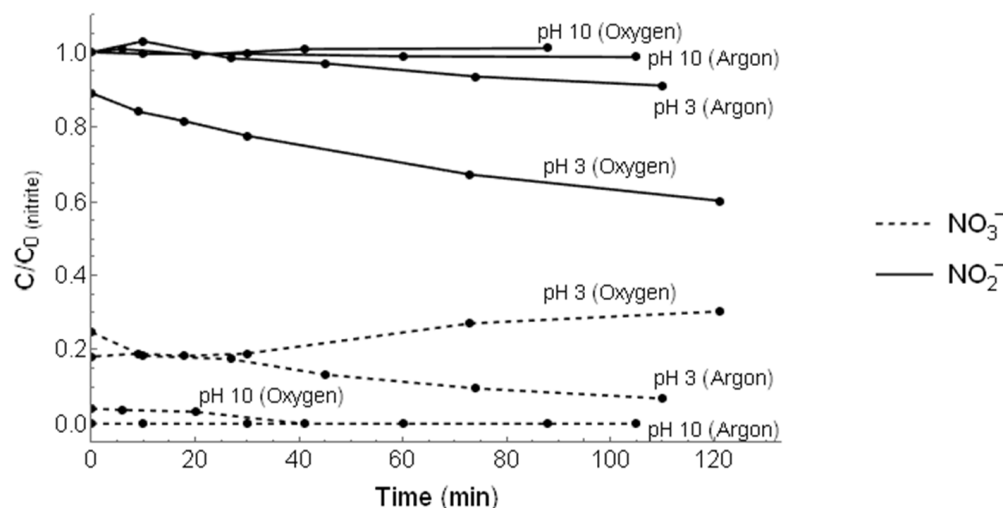


Figure 3. NO_3^- (dashed lines) and NO_2^- (solid lines) profiles vs. time obtained after the irradiation of NO_2^- (1.5 mM). The reaction was performed at pH 3 and pH 10 with and without O_2 .

In an aqueous solution, nitrous acid (HNO_2) exists in equilibrium with NO_2^- with a $\text{pK}_a = 3.4$ (Equation (3)).



When exposed to 355 nm irradiation, both species undergo a similar photolytic process, with the acid form exhibiting a higher quantum yield ($\phi_{355 \text{ nm}}^{\text{HNO}_2} = 0.4$ vs. $\phi_{355 \text{ nm}}^{\text{NO}_2^-} = 0.025$ respectively) [7,20]. This disparity in quantum yields could explain the observed oxidation only in acidic conditions (Equations (4) and (5)).



3.3. Irradiation of $\text{NH}_3/\text{NH}_4^+$

The removal of aqueous $\text{NH}_3/\text{NH}_4^+$ via irradiation was observed at a high pH (Figure 4) in the presence of oxygen in contrast to the NO_2^- oxidation that only took place at a low pH (Figure 3). At pH 10, 72% of $\text{NH}_3/\text{NH}_4^+$ (1.5 mM) was converted mainly into an unidentified compound. The concentrations of NO_3^- and NO_2^- were low and constant throughout the experiment, suggesting that these compounds were reaction intermediates in a steady-state mechanism. The reaction was not observed at a pH lower than 7 (kinetic curves not shown) or in the absence of O_2 .

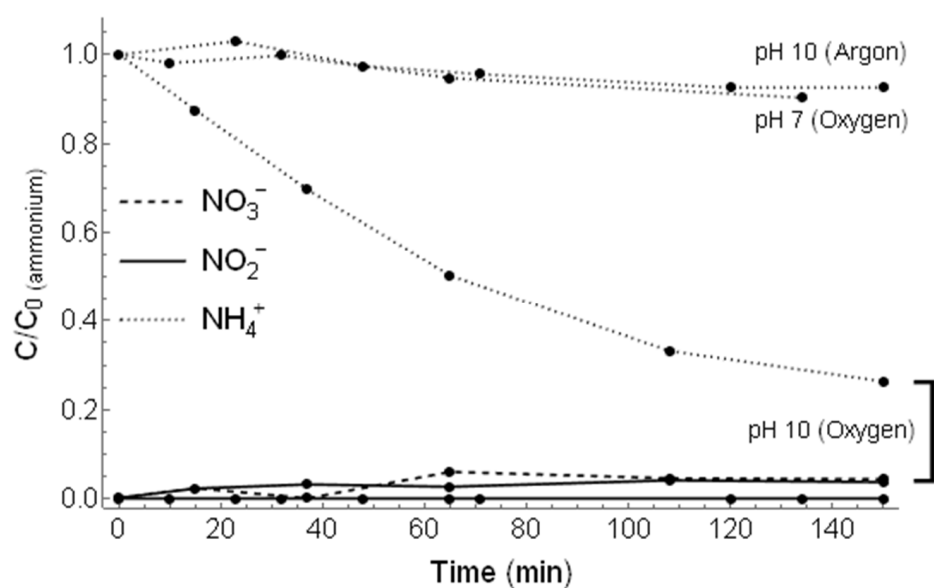
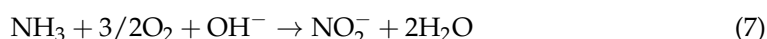


Figure 4. NH_4^+ (dotted lines), NO_3^- (dashed lines) and NO_2^- (solid lines) profiles vs. time for the irradiation of $\text{NH}_3/\text{NH}_4^+$ (1.5 mM) in oxic and anoxic conditions. The solutions were purged with oxygen and argon, respectively.

Unlike NO_3^- and NO_2^- , $\text{NH}_3/\text{NH}_4^+$ do not absorb light in the emission range of the medium-pressure mercury lamp. Therefore, the direct photolysis of these species was ruled out. Nevertheless, hydroxyl radical (HO^\bullet) can be generated via direct photolysis of water at 254 nm with a quantum yield of 0.08 for the HO^\bullet formation [21]. The oxidation of NH_3 via a reaction with HO^\bullet was reported before, and it led to the formation of NO_2^- . It was suggested that the initial reaction proceeds with the hydrogen abstraction with HO^\bullet yielding the key intermediate NH_2^\bullet (Equation (6)) [22].



Besides light, O_2 is a necessary reagent, so Equation (7) was proposed to be the overall reaction here [23]. Also, the $\text{NH}_4^+/\text{NH}_3$ acid–base equilibrium pK_a is 9.25, which explains that the oxidation was observed at a more alkaline pH where NH_3 is the main species.



It is postulated that after the initial oxidation of NH_3 into $\text{NO}_3^-/\text{NO}_2^-$, both compounds reacted to produce N_2/NO_x (see next section), which would explain the total nitrogen decrease. This could be described with a two-step consecutive reaction mechanism where the first reaction (NH_3 oxidation) is much slower than the second reaction (N_2/NO_x generation), producing a steady-state low concentration of NO_3^- and NO_2^- during the reaction.

3.4. Simultaneous Irradiation of NO_2^- and $\text{NH}_3/\text{NH}_4^+$

The simultaneous removal of aqueous NO_2^- and NH_3 was achieved via irradiation at pH 10 without the detection of NO_3^- (Figure 5). Both compounds (0.75 mM) were removed by 75% in 2.5 h. The kinetic curves obtained for NO_2^- and $\text{NH}_3/\text{NH}_4^+$ were almost identical, indicating that the reaction stoichiometry between NO_2^- and $\text{NH}_3/\text{NH}_4^+$ was 1:1. Moreover, the experimental data adjusted very well to a rate equation with a partial first order for NO_2^- and also partial first order for NH_3 ($\nu = k [\text{NO}_2^-] [\text{NH}_3]$, $k = 0.5 \text{ M}^{-1} \text{ seg}^{-1}$, $R^2 = 0.9994$).

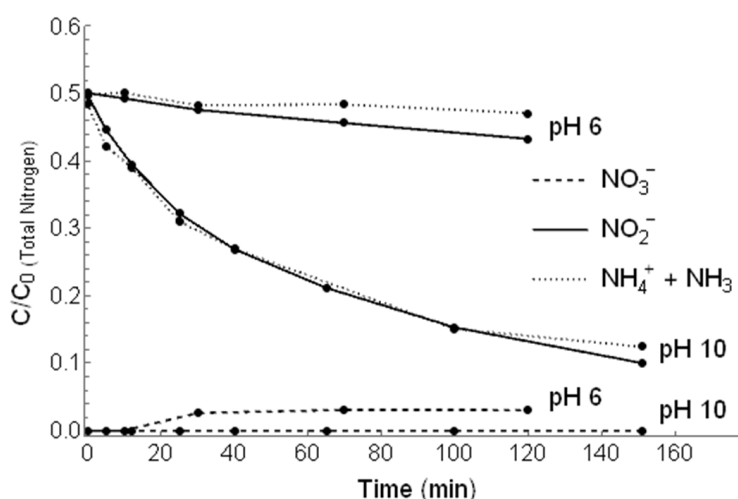


Figure 5. NO_3^- (dashed lines), NO_2^- (solid lines) and $\text{NH}_3/\text{NH}_4^+$ (dotted lines) profiles vs. time for the irradiation of NO_2^- and $\text{NH}_3/\text{NH}_4^+$ at varying pH conditions. The initial total nitrogen concentration (C_0) was 1.5 mM. The solution was purged with argon.

At pH 6, the reaction was significantly slower, and the formation of NO_3^- was evidenced as a reaction product without a significant total nitrogen removal. This reaction dependence on pH suggested that NH_3 , not NH_4^+ , is the reactant that leads to nitrogen removal.

The mechanism of the photochemical reaction between NH_3 and NO_2^- can be analyzed considering the mechanism of the thermal reaction. One of the key intermediates proposed in the thermal reaction is dinitrogen trioxide (N_2O_3). NH_3 reacts with N_2O_3 (Equation (8)) through a Substitution Nucleophilic Bimolecular reaction ($\text{S}_{\text{N}}2$) (Figure 6A) [24] where NH_3 is the nucleophile, N_2O_3 the electrophile and NO_2^- the leaving group.

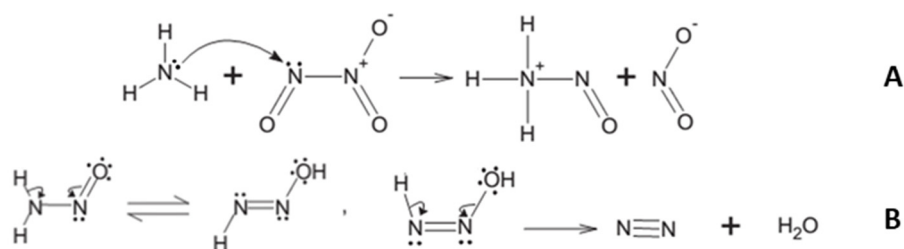


Figure 6. Substitution Nucleophilic Bimolecular reaction between NH_3 and N_2O_3 (A) and H_2NNO isomerization and dissociation (B).

The transient compound, H_3NNO^+ , quickly converts into nitrosamine (H_2NNO) (Equation (9)) [24].



And H_2NNO isomerizes into HNNOH , which dissociates into the final products N_2 and H_2O (Equation (10)) [24] (Figure 6B).



As in the thermal reaction, N_2O_3 could also be postulated as an intermediate for the photochemical reaction [25]. The final steps of the mechanisms leading to N_2 would be the same as stated above, but the difference would lie in how N_2O_3 is formed. In the

thermal reaction, N_2O_3 is postulated to be generated by the condensation of two molecules of HNO_2 (Equation (11)) [24].

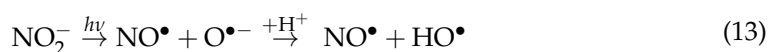


In fact, HNO_2 and NH_3 are the postulated reagents for the thermal reaction where the reaction rate increases at a lower pH [24]. On the contrary, in the photochemical reaction, the postulated reagents are NO_2^- and NH_3 , and as shown here, the reaction takes place in alkaline media.

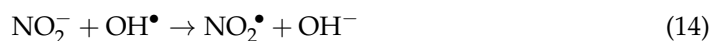
The formation of N_2O_3 via irradiation could be explained by the reaction between NO^\bullet and NO_2^\bullet (Equation (12)) [8].



where NO^\bullet is obtained in the photochemical primary process of NO_2^- irradiation (Equation (13)) [26]:



and NO_2^\bullet is generated by the oxidation of NO_2^- by OH^\bullet (Equation (14)) [27].



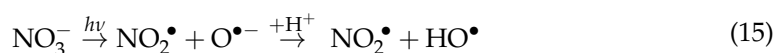
Another important difference is that in the thermal process, the kinetic mechanism is near-second-order in the HNO_2 concentration [24], whereas we showed here that in the irradiation process, the reaction was first-order in the NO_2^- concentration.

We did not observe a significant reaction in the dark. This could be due to the relatively low total nitrogen concentration (about 1.5 mM) used in these experiments. The thermal reaction is reported to have occurred mainly at concentrations above 100 mM¹¹. This agrees with the different reaction mechanisms indicated above.

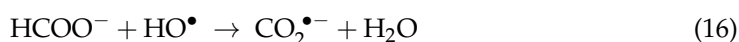
3.5. Irradiation of NO_3^- in the Presence of Formic Acid

As shown in previous sections, the irradiation of NO_3^- and NO_2^- with a medium-pressure mercury lamp produces reactive nitrogen species (RNS) as intermediates, which in turn yields NO_2^- as the main product regardless of the initial conditions of pH and oxygenation. To achieve further nitrogen reduction and eventually eliminate it, it is necessary to add another reactant as an electron donor, such as an organic compound.

This is possible because the irradiation of NO_3^- and NO_2^- , besides RNS, produces reactive oxygen species (ROS), which are scavenged by organic compounds that are oxidized and mineralized in this way. HO^\bullet is the main ROS produced as a consequence of the irradiation of NO_2^- and NO_3^- (Equations (13) and (15), respectively). Therefore, this irradiation process has also been proposed for the removal of contaminants of emerging concern (CECs) [14].



In particular, it is known that formic acid is oxidized by HO^\bullet , yielding $CO_2^{\bullet-}$ as the first intermediate (Equation (16)) [28].



The irradiation of NO_3^- in the presence of formic acid yielded NH_3 and a loss of total nitrogen at pH 10 (Figure 7). In the beginning of the reaction, a transient peak of NO_2^- concentration was observed along with a quick fall of the NO_3^- concentration. Then, NH_3 appeared after a lag period in which a minimum of total nitrogen was observed. This suggested the presence of another nitrogen intermediate that was different from the three main DINs and that was converted into NH_3 more slowly.

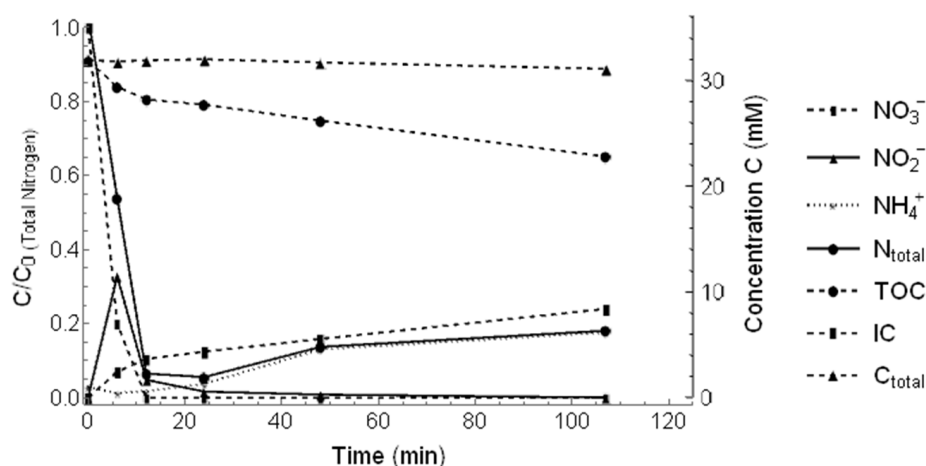


Figure 7. Irradiation of NO_3^- (1.5 mM) at pH 10 with 30 mM formic acid. The solution was continuously purged with argon.

NO_3^- removal with formic acid was faster than in the simple irradiation (Section 3.1). Also, the total nitrogen was removed faster than in the simultaneous irradiation of NO_2^- and NH_3 (Section 3.4), evidencing a different mechanism for nitrogen removal. Similar reaction rates were obtained at pH 3 with formic acid. This was another significant difference compared to the irradiation without the electron donor, which had a marked dependence on the pH as shown before.

It is suggested that this new mechanism and the nitrogen intermediates could be initiated by the reaction between NO^\bullet and $\text{CO}_2^{\bullet-}$ (Equation (17)), which are the products of the photolysis of NO_2^- (Equation (13)) and the oxidation of formic acid (Equation (16)), respectively [28].



The oxidation of formic acid was also confirmed with the measurement of total organic carbon (TOC). During the reaction, the TOC was reduced steadily along with the formation of inorganic carbon (IC), which showed the mineralization of the formic acid (Figure 7).

Formate has already been tested for the removal of nitrate from groundwater [29], indicating that the environmental application is potentially possible.

4. Conclusions

The irradiation of the principal DIN compounds (NO_3^- , NO_2^- and $\text{NH}_3/\text{NH}_4^+$) was performed separately at a relatively low concentration (1.5 mM) with a medium-pressure mercury lamp with main emission bands between 313 and 436 nm. The interconversion of DIN compounds was observed mainly in alkaline media (pH 10–11). In these conditions, it was found that NO_3^- is fully converted into NO_2^- following first-order reaction kinetics, and NH_3 was removed from the solution in the presence of oxygen, also yielding a minimum amount of NO_3^- and NO_2^- . Interestingly, when NO_2^- and NH_3 were irradiated simultaneously, both were removed from the solution in a 1-to-1 mol proportion without the requirement of any other reactant. Finally, NO_3^- was reduced to NH_3 only after the addition of formic acid as an electron donor, also yielding the removal of the DINs from the solution.

The required alkaline media suggested NH_3 as the active compound instead of NH_4^+ , and in the case of NO_3^- irradiation, it suggested the presence of a reaction intermediate, probably peroxynitrite (ONOO^-), which is unstable in an acidic pH.

It was demonstrated that the DINs could be removed from the solution without introducing a catalyst and by applying a light source emitting in the UV A/B range; therefore, solar irradiation could eventually be applied also. The strategy for DIN removal via irradiation would be to have NO_3^- and/or NO_2^- mixed with NH_3 at pH 10–11. If NO_3^- and NO_2^- are initially absent, they can be obtained via irradiation of NH_3 in the presence

of oxygen. On the other hand, if NH_3 is initially absent, it can be obtained via the reduction of NO_3^- and/or NO_2^- adding an electron donor such as formic acid as shown in this work.

In conclusion, our study demonstrates that direct UV irradiation of DINs presents a promising removal protocol, serving as a valuable complementary approach to enhance existing techniques. Its main advantages lie in its minimal supply requirements, as it solely relies on a UV light source (the protocol can be enhanced by the addition of formate) and eliminates the need for catalysts. On the other hand, it is suggested that formate was oxidized by RNS and ROS produced by the irradiation of nitrate and nitrite. RNS and ROS oxidation have also been proposed as degradation mechanisms of CECs achieving the removal of nitrate and nitrite at the same time.

By offering a simple and sustainable alternative, our findings encourage further exploration and integration of direct UV irradiation in DIN removal strategies, paving the way for more efficient and environmentally friendly pollutant mitigation practices.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/chemengineering7050079/s1>, Figure S1: Absorption UV–vis spectra of NO_3^- and NO_2^- measured at pH 10.5 and emission spectrum of the medium-pressure Hg lamp.

Author Contributions: Conceptualization, A.M.S. and N.Q.; methodology, A.M.S.; formal analysis, A.M.S. and N.Q.; investigation, A.M.S.; resources, N.Q.; writing—original draft preparation, A.M.S.; writing—review and editing, N.Q.; project administration, N.Q.; funding acquisition, N.Q. All authors have read and agreed to the published version of the manuscript.

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