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UV-activated persulfate oxidation of the insensitive munitions compound 2,4-dinitroanisole in water: Kinetics, products, and influence of natural photoinducers

Yan Yang[a], Yuefei Ji[a,*], Peizeng Yang[a], Lu Wang[a], Junhe Lu[a,*], Corinne Ferronato[b], Jean-Marc Chovelon[b]

[a] College of Resources and Environmental Sciences, Nanjing Agricultural University, Nanjing 210095, China
[b] Univ Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON, F-69626, Villeurbanne, France

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ABSTRACT

2,4-Dinitroanisole (DNAN) is an emerging organic contaminant that may pose potential risks to both human health and ecological system. In this contribution, we attempt to investigate the degradation of DNAN in water by UV-based advanced oxidation processes, including UV/H_2O_2 and UV/persulfate (UV/PS). Both UV/H_2O_2 and UV/PS were capable of degrading DNAN; however, the latter appeared to be more efficient than the former, especially when high dosage of peroxide was utilized. An increase in the degradation rate of DNAN was observed with increasing concentration of PS. Kinetic modeling based on the assumption of steady-state concentration of sulfate radical ($SO_4{\cdot}^-$) underestimated the removal of DNAN, most likely due to an decrease in PS concentration and significant formation of by-products. Time-dependent evolution of 2,4-dinitrophenol (2,4-DNP), the major intermediate product of DNAN, can be well described by a sequential kinetic model. Solution pH had negligible impact on DNAN degradation. The presence of natural occurring photoinducers, such as Suwannee River fulvic acid (SRFA) and nitrate (NO_3^-), inhibited the degradation of DNAN appreciably, possibly due to light screening and/or radical scavenging effects. However, high concentration of NO_3^- mitigate the inhibitory effect, presumably due to the reactive nitrogen species (RNS) generated by NO_3^- photolysis. Experimental results suggest that DNAN was amenable to oxidation by UV/PS; however, the treatment efficiency could be remarkably influenced by natural photoinducers present in waters such as natural organic matter (NOM) and NO_3^-.

1. Introduction

2,4-Dinitroanisole (DNAN) is an insensitive munitions compound that has been used by the defense industry as a substitute for more sensitive explosives (e.g., 2,4,6-trinitrotoluene, TNT) [1]. Due to large scale production and deployment in the field, environmental fate and ecotoxicological risks associated with DNAN has received growing concerns among scientific communities and regulatory agencies [1]. DNAN can be transformed in the environment by both biotic and abiotic processes, such as biodegradation [2–4] and photolysis [5,6]; however, these natural attenuation processes generally occur at slow rates. The presence of DNAN in natural environmental compartments, such as soil and groundwater, requires appropriate remediation or treatment, because recent studies have demonstrated that DNAN is toxic to organisms such as algae, bacteria, and earthworms [7,8]. While reductive transformation of DNAN, either by zero-valent iron (ZVI) [9] or by Fe-Cu bimetal system [10], has a potential for removing DNAN from water, the resulting by-products with amine functional group(s) requires further treatment. Transformation of DNAN by oxidative approaches, especially those widely utilized in water and wastewater treatment (e.g., O_3, UV/H_2O_2, and O_3/H_2O_2), is still scarcity and warrants further investigations.

UV activated persulfate system (UV/PS) is a promising advanced oxidation process (AOP) capable of generating reactive sulfate radicals ($SO_4{\cdot}^-$) by photochemically cleaving peroxide bonds upon radiation [11]. $SO_4{\cdot}^-$ is a single-electron oxidant with a redox potential of 2.5–3.1 V (depending on pH), which reacts with organics at rate constants normally ranging from 10^6 to $10^9\,M^{-1}\,s^{-1}$ [12,13]. UV/PS performs in a manner analogous to UV/H_2O_2 which produces hydroxyl radicals ($HO\cdot$); however, the former has a comparatively higher quantum yield of radicals (i.e., 1.4 for UV/PS vs. 1.0 for UV/H_2O_2) [14]. This is because the bond energy of PS peroxide bond is $140\,kJ\,mol^{-1}$, much lower than that of H_2O_2 ($213.3\,kJ\,mol^{-1}$) [15]. In addition, lengths of the peroxide bond of PS and H_2O_2 are 1.497 Å and 1.453 Å, respectively, implying that PS is more likely to be photo-

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* Corresponding authors.
E-mail addresses: yuefeiji@njau.edu.cn (Y. Ji), jhlu@njau.edu.cn (J. Lu).

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activated to produce reactive radicals [15,16]. $SO_4\cdot^-$ possess several advantages over $HO\cdot$ such as longer life-time and higher selectivity [17]. It is widely accepted that $SO_4\cdot^-$ reacts with contaminants primarily via single-electron transfer pathway [13], which enable it being less quenched by water constituents, such as natural organic matter (NOM) and bicarbonate (HCO_3^-) [17]. In addition, application of UV/PS process may also be advantageous over other UV-based AOPs, such as UV/TiO_2, for organic pollutants mineralization. For example, in a recent study conducted by Hazime et al. [18], quantity of photoproducts in UV/$K_2S_2O_8$ system was found to be low comparing to UV/TiO_2 process, and the presence of PS improved the mineralization of the fungicide imazalil. Furthermore, when visible light and sunlight are used as irradiation source, this technology will be more economically competitive [19]. Previous studies have demonstrated the effectiveness of UV/PS in removal of a broad range of contaminants in water, including pesticides [15,20,21], pharmaceuticals and personal care products (PPCPs) [22–24], endocrine disrupting chemicals (EDCs) [25], flame retardants [26]; cyanotoxins [27,28], and odorous compounds [29,30] (Table S1, Supplementary material, hereafter SM).

While DNAN degradation by direct photolysis with UV radiation has been documented recently [5,6]; little information is available concerning its elimination by UV-based AOPs, such as UV/PS process. $SO_4\cdot^-$ generated in activated PS systems has a potential to transform nitroaromatic compounds (NACs), leading to the formation of a suite of intermediate products with unknown ecological toxicity [31]. In particular, recent studies revealed a denitration-renitration mechanism through which certain NACs, including nitrobenzene and nitrophenol, was transformed in $SO_4\cdot^-$-based AOPs [32,33]. Therefore, kinetic and mechanistic studies on the formation and transformation of intermediates are highly essential to accurately predict potential risks associated these by-products. The UV/PS process is also expected to be significantly impacted by naturally occurring species present in raw waters [21,22]. These species, especially those serve as photoinducers such as natural organic matter (NOM) and nitrate (NO_3^-), are capable of screening UV light and/or scavenging reactive radicals by acting as inner filters and/or radical scavengers, thus reducing the removal efficiency of target compounds [34,35]. Therefore, understanding the effects of these constituents may provide insights into the efficacy of UV/PS performed under environmentally relevant conditions.

In the present study, we attempted to assess the feasibility of employing UV/PS to remove DNAN in water. The motivation of this work is to explore a viable method to destroy or eliminate DNAN and other munitions compounds that can potentially contaminate surface water and groundwater. Therefore, the main objectives of this contribution are (1) to evaluate the efficacy of loss of DNAN in UV/PS process; (2) to study the intermediate products formed during DNAN transformation from both kinetic and mechanistic point of view; (3) to elucidate the effects of two natural photoinducers, i.e., NOM and NO_3^-, on the removal of DNAN by UV/PS process.

2. Materials and methods

2.1. Chemicals and materials

All chemicals were of reagent grade or higher purity. Dinitroanisole (DNAN), 2,4-dinitrophenol (2,4-DNP), 2,4,6-trinitrophenol (2,4,6-TNP), 2-methoxy-5-nitrophenol (2-MeO-5-NP), *para*-chlorobenzoic acid (*p*CBA), and *m*-toluic acid (mTA) were purchased from Sigma-Aldrich (St, Louis, MO, USA). Acetonitrile (ACN), methanol (MeOH) and formic acid used for the chromatographic mobile phase were HPLC grade (Burdick & Jackson, Muskegon, MI). Suwannee River fulvic acid (SRFA, 2S101F) was obtained from the International Humic Substances Society (IHSS, St. Paul, MN, USA). All the stock solutions were prepared by dissolving the chemical agents into Milli-Q water (18 MΩ cm) prepared from a Milli-Q water purification system (Millipore, Bedford, USA) and used within one week.

2.2. Photochemical reactor

Photochemical experiments were performed using a merry-go-round photoreactor (BL-GHX-V, Bilang, Shanghai) equipped with a 15 W low pressure mercury (LP-Hg) lamp emitting predominantly monochromatic light at 254 nm. The incident photon irradiance was actinometrically determined to be 6.67×10^{-8} Einstein $L^{-1} s^{-1}$ following a procedure described by Canonica et al. [36]. The LP-Hg lamp was centered in a quartz cooling jacket connected to a recirculating cooler (BL-T-1000S, Bilang, Shanghai) to maintain the temperature at approximately 20 °C.

2.3. DNAN degradation by UV, UV/H_2O_2, and UV/PS processes

UV photolysis and UV-based advanced oxidation (UV/H_2O_2 or UV/PS) experiments were conducted in a series of uncapped cylindrical quartz tubes (22 mm i.d., 60 mL volume) containing 50 mL 40 μM DNAN reaction solutions. The tubes were placed vertically outside the jacket at a fixed distance to ensure uniform photon radiation. For UV/H_2O_2 and UV/PS, appropriate amounts of peroxide were added to the reaction solutions prior to UV irradiation. The reaction solutions were homogenized by magnetically stirring during UV irradiation. Dark controls wrapped with aluminum foil were also carried out under identical conditions. To investigate the effects of natural photoinducers, different concentrations of SRFA and NO_3^- were spiked into the reaction solutions. Initial pH of the solution was adjusted by 0.1 M NaOH or $HClO_4$ to preset values. No buffer was used to avoid potential reactions between buffer species (e.g., HCO_3^-, HPO_4^{2-}) and reactive radicals [21]. Aliquot samples were withdrawn at predetermined time intervals and quenched immediately with 0.1 mL MeOH, a well-known radical quenching agent [37]. All the experiments were carried out in duplicates to assure accurate data acquisition and error bars in figures represent the standard deviations.

2.4. Determination of second-order rate constants

Second-order rate constants for reaction of $SO_4\cdot^-$ with DNAN and 2,4-DNP were determined by competition kinetic method using *p*CBA and mTA as reference compound, respectively, following a procedure described by Xiao et al. [38]. Detailed experimental procedures are provided in Text S1, SM. The second-order rate constant for reaction of $SO_4\cdot^-$ with substrate, $k_{SO4\cdot^-,S}$, is calculated by the following equation:

$$k_{SO_4^{\circ-},S} = \frac{k_{obs,UV/PS/S} - k_{obs,UV/S}}{k_{obs,UV/PS/Ref} - k_{obs,UV/Ref}} k_{SO_4^{\circ-},Ref} \quad (1)$$

where $k_{obs,UV/PS/S}$ and $k_{obs,UV/PS/Ref}$ are the observed pseudo-first-order rate constants (s^{-1}) of substrate and reference compound in the UV/PS process, respectively; $k_{obs,UV/S}$ and $k_{obs,UV/Ref}$ are the direct photolysis rate constants (s^{-1}) of substrate and reference compound, respectively; $k_{SO4\cdot^-,Ref}$ is the second-order rate constant for reaction of $SO_4\cdot^-$ with reference compound ($M^{-1} s^{-1}$).

2.5. Analytical methods

Molar adsorption coefficients of DNAN, 2,4-DNP, and PS were recorded by a Cary 50 Conc UV–vis spectrophotometer (Varian, Palo Alto, CA, USA) using quartz cuvettes with 1 cm path length. Solution pH was measured by a combined glass electrode (E-201-C, Leici) connected to a PHS-3CW microprocessor pH/mV meter (Bante instrument Co. Ltd, Shanghai). Total organic carbon (TOC) of the reaction solution was quantified using a TOC-5050A analyzer (Shimadzu, Japan).

Concentrations of DNAN, 2,4-DNP, 2,4,6-TNP, 2-MeO-5-NP, *p*CBA, and mTA were analyzed by a Hitachi L-2000 high performance liquid chromatography (Hitachi, Japan) equipped with an L-2200 autosampler, an L-2130 binary pump, and an L-2455 diode array detector