

The Effects of Photocatalyst and Solution Co-Contaminants on Photocatalytic Oxidation of 1,3- Dinitrobenzene in Aqueous Semiconductor Oxide Suspensions

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Abstract

Heterogeneous photocatalysis of 1,3-dinitrobenzene (DNB) using simulated solar irradiation in the presence of semiconductor oxides was studied. Comparison of TiO₂ and ZnO showed that the former was a more efficient photocatalyst for the degradation of DNB. The addition of potential environmental co-contaminants such as acetic acid, fulvic acid and seawater salts to the DNB solutions all inhibited the DNB degradation rate. The addition of hydroxyl radical-generating compounds, including H₂O₂ and NaNO₃, to the DNB solutions both slightly reduced the DNB degradation rate, indicating that hydroxyl radical generation is not a rate limiting step in the overall reaction process. The use of 5 volume % acetone cosolvent slowed the degradation rate, however for 15 volume % acetone despite the slower relative rate of destruction, the higher concentrations of DNB provided higher mass destruction rates.

Keywords: Heterogeneous photocatalysis; Titanium dioxide; Dinitrobenzene; Advanced oxidation

Introduction

Heterogeneous photocatalytic oxidation is an advanced oxidation process that uses electrons and holes generated by the irradiation of a semiconductor with appropriate wavelength light to generate oxidizing species in aqueous solution. Titanium dioxide (TiO₂) is a common photocatalyst with a band gap of 3.2 eV and which can produce electron and hole pairs when irradiated by light having a wavelength less than 387 nm [1,2]. There is growing interest in the photocatalyst zinc oxide (ZnO), which despite its less favorable band gap of 3.37 eV has demonstrated desirable activity under visible light [3]. The conduction band electrons and valence band holes formed during irradiation of the semiconductor can participate in reduction and oxidation reactions, respectively, through interactions between charged species at the solid surface and components in solution. In aqueous solution, hydroxyl radicals may be produced from superoxide anions formed by oxygen reduction or by oxidation of water [4]. The hydroxyl radical is a strong and nonselective oxidizing agent which can degrade many recalcitrant waste compounds. Heterogeneous photocatalytic oxidation has been studied for remediation of many classes of wastewater contaminants, such as chlorinated compounds, aromatics, pharmaceutical compounds, hydrocarbons and dyes [5].

The release of nitroaromatic compounds to the environment during the production, storage or decommissioning of explosives can produce contaminated water or soil which must be treated as hazardous waste. Nitroaromatic compounds have shown resistance to oxidative degradation [6] and there is ongoing work to understand the reaction mechanism and improve the effectiveness of treatment processes. Chen et al. used oxygen-isotope labelled reagents to study the hydroxylation pathway of several aromatic compounds during photocatalysis [7]. They observed that both O₂ and H₂O contributed oxygen to the products, but the proportion from each source depended strongly on reaction conditions.

Substitution on the benzene ring is another important consideration for the initial hydroxylation step of aromatics. Hydroxyl groups on the benzene ring activate the ring for electrophilic attack at the ortho and para positions while nitro groups on the benzene

ring deactivate the ring for electrophilic attack and is meta-directing. Priya and Madras [8] observed that the initial photodegradation rates of several nitroaromatic compounds increased in the order of 1, 3-dinitrobenzene < nitrobenzene < 2,4-dinitrophenol < 3-nitrophenol < 2-nitrophenol < 4-nitrophenol. Dillert [9] compared several related compounds and observed that reactivity via photo-oxidation increased in the order of 2, 4, 6-trinitrotoluene < dinitrobenzenes < dinitrotoluenes < nitrobenzene. Several studies of photocatalytic oxidation of nitrobenzene using TiO₂-based catalysts have been published [6,8-15] but there are fewer publications addressing 1, 3- dinitrobenzene (DNB) photocatalysis [9,16,17]. In this work, oxidation of DNB was studied as a surrogate for a common explosive, trinitrotoluene (TNT). DNB was chosen because it has shown a slower photocatalytic degradation rate than several other nitroaromatic and nitrophenol compounds used as model compounds for explosives and therefore was expected to be a better indicator for treatment of explosive-contaminated water.

To develop an effective waste treatment method, it is important to understand the impacts of both reaction conditions and potential co-contaminants in the waste on the overall oxidation process. In this work, photocatalytic oxidation of DNB was studied using solutions modified by the addition of two common co-contaminants (organic matter and salts) which can potentially enhance or inhibit the oxidation process. DNB degradation was also studied using solutions modified by the addition of two reagents that can enhance hydroxyl radical production. The results provide additional insight into ways to improve

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the effectiveness of heterogeneous photocatalysis for remediating nitroaromatic compounds in aqueous waste streams.

Experimental

Materials and methods

1, 3-dinitrobenzene (97%) (DNB) and zinc oxide (Sigma Aldrich) were used as received. Degussa P25 TiO₂ was provided by the manufacturer. Solutions were typically prepared by dissolving 50 mg/L of DNB in MilliQ water with the aid of sonication and heating. Photoreactions were performed in 16.5 mL glass vials which had been previously soaked in 10% HCl, rinsed and dried, to prevent DNB from adsorbing on the glass. Photocatalyst was weighed into each tube, 10 mL of DNB solution was added and the vial was sealed with an aluminum foil-lined cap. The tubes were sonicated before reaction to completely disperse the TiO₂. Photoreactions were performed in a light box containing six UVA-340 lamps (Q-Panel) providing an irradiance of 17.5 W/m² measured with a radiometer. Using ferrioxalate actinometry the photon absorption rate of solution inside the reaction tube was estimated to be 5.0 × 10⁶ E/min. To prevent settling of the TiO₂ during irradiation, the vials were stabilized on the bed of an orbital shaker and shaken at 150 rpm.

Reaction progress was monitored by quantifying the loss of DNB from the solution. After irradiation, the reaction solution was immediately transferred to a 50 mL amber vial and 5 mL of toluene was added to extract unreacted DNB into the organic phase. The amber vial was vortexed for a minimum of one minute. 5 µL of the extracted toluene phase was added to 1 mL of pure toluene in a GC vial. DNB was quantified using a Thermo Trace GC with ECD detection, using a 30 m Restek RTX-5 column (0.32 mm ID, 0.25 µm film thickness). One µL volumes of standard or sample extracts were injected with a 10:1 split ratio and injection port temperature of 230°C. The column temperature was initially held for 1 minute at 70°C, then ramped at 20°C/minute to a final column temperature of 280°C which was held for 6 minutes. Total GC run time was 17.50 minutes. The ECD temp was 350°C, with a makeup gas flow of ultrapure nitrogen at 45 mL/minute. Calibration standards were prepared in pure toluene.

Experiments were performed under various conditions to determine the impact of potential environmental contaminants on DNB degradation and to identify potential enhancements in reaction effectiveness. Initial experiments were performed to screen different mass loadings of TiO₂ and ZnO photocatalyst. The effect of potential environmental conditions was studied by adding common co-components to the DNB solution. Acetic acid was added to represent low pH organic contaminants. Surface water typically contains humic substances, a complex mixture of compounds formed from the decay of plant matter and microbial biomass. Fulvic acid was selected to represent the lower molecular weight components of humic substances and was added to DNB solutions to create solutions resembling contaminated surface water. The composition of fulvic acid depends on the local environment, and Suwannee River Fulvic Acid Standard was used as a representative standard. It is a standard reference material representative of terrestrially-impacted environments, available from the International Humic Substances Society, and is commonly used in aquatic studies. DNB solutions were also prepared in simulated sea water to model spills in brackish or saline water. Simulated sea water was prepared by mixing appropriate amounts of several sodium and potassium salts in MilliQ water to match the composition of sea water. To study means to enhance the reaction, hydrogen peroxide and sodium nitrate were added to the DNB solutions. When irradiated,

these compounds are known to generate hydroxyl radicals which could contribute to DNB oxidation. Finally, the possibility of increasing DNB disposal rates by treating more concentrated DNB solutions was investigated by acetone as a cosolvent to increase DNB solubility.

Results and Discussion

Stability of DNB under control conditions

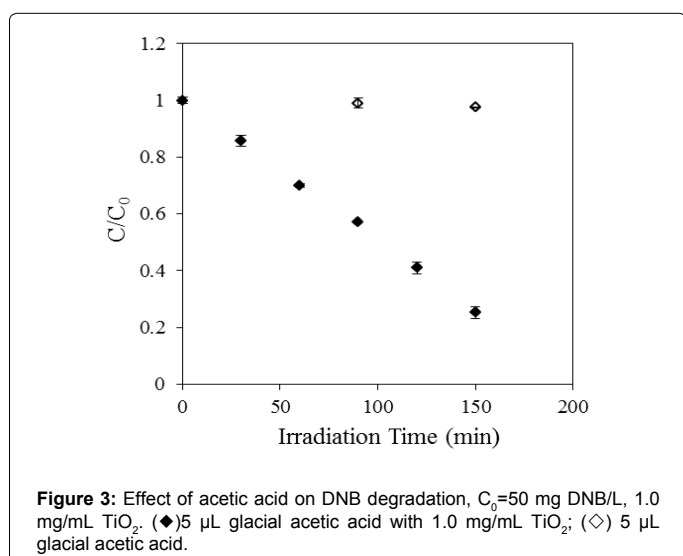
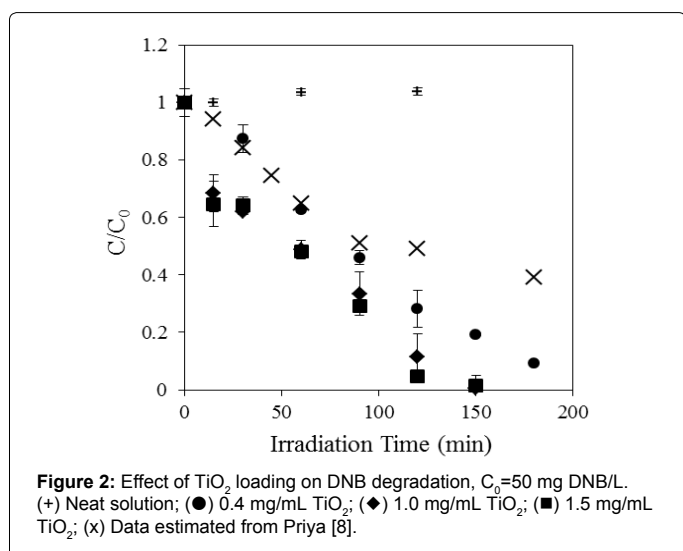
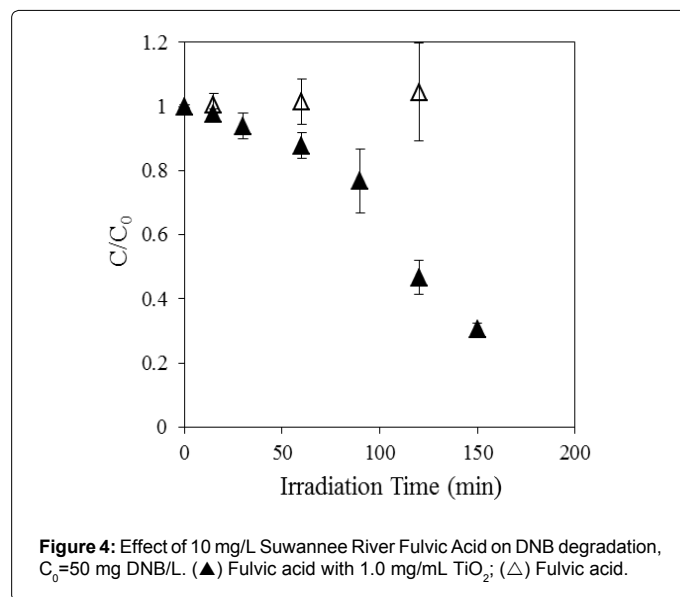
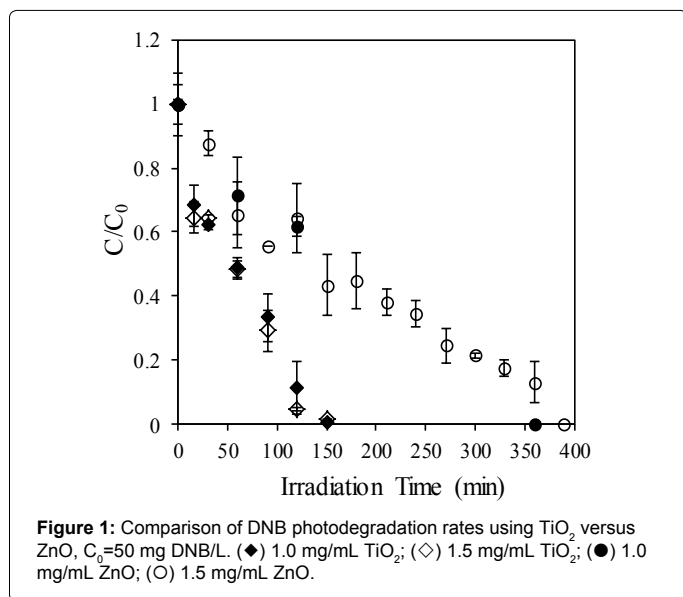
Stability studies were initially performed over a period of 50 hours and confirmed that DNB was stable in solutions containing TiO₂ without irradiation and under the simulated solar light in neat solutions.

Effect of photocatalyst and photocatalyst loading: Figure 1 shows that TiO₂ is a more active photocatalyst for DNB oxidation than ZnO. A similar observation has been reported for photocatalytic oxidation of nitrobenzene [10]. In addition, for each semiconductor, a catalyst loading of 1.0 mg/mL versus 1.5 mg/mL caused little change in DNB degradation. Figure 2 shows that a lower TiO₂ loading of 0.4 mg/mL reduced the DNB degradation rates. Bhatkhande [13] observed a similar optimal TiO₂ loading for photocatalysis of nitrobenzene. This behavior is attributed to the balance between catalyst surface area and light penetration. For low catalyst loadings, higher reaction rates with increased catalyst loading is attributed to increased catalyst surface area. However at high catalyst loadings, light penetration becomes blocked, limiting the active reaction volume and reducing overall reaction rates despite the increase in catalyst surface area [4]. Based on these results, all further experiments were performed using a TiO₂ loading of 1.0 mg/mL.

Effect of potential environmental contaminants

Addition of acetic acid: The addition of 5 µL of glacial acetic acid to each photovial before reaction decreased the rate of DNB degradation in the presence of TiO₂. As shown in Figure 3, with the addition of acetic acid only 80% of the DNB reacted after 150 minutes of irradiation, whereas without the added acid DNB was completely degraded within that time. This is consistent with observations of Kamble [17] that neutral solutions of DNB degrade faster under UV irradiation in TiO₂ slurries than either acidic or basic solutions. Furthermore, Araña observed that acetic acid significantly altered adsorption behavior of catechol and resorcinol through interactions with the surface oxides of titanium dioxide [18]. Using oxygen saturated solutions and UV irradiation, the presence of intermediate concentrations of acetic acid enhanced degradation of catechol and resorcinol, yet higher acid concentrations impeded degradation.

Addition of Suwannee River fulvic acid standard: The addition of 10 mg/L of Suwannee River Fulvic Acid Standard to DNB solutions yielded a DNB degradation rate similar to that observed for the addition of acetic acid, as shown in Figure 4. The presence of humic substances can inhibit DNB degradation through mechanisms including radical scavenging, surface adsorption and light absorption. This was observed for the oxidation of dichlorophenol in the presence of humic acid [19]. However, Mihas observed the opposite behavior with the addition of 10 mg/L of humic acid to 1 mg/L solutions of 2,4- dinitrotoluene and noted an enhanced photolysis rate in the presence of humic acid [12]. The catalytic and inhibitive effects observed for humic substances added to solutions of different nitroaromatics undergoing heterogeneous photocatalysis and photolysis is consistent with a complex reaction mechanism that involves solution and surface effects that are highly dependent on the solute, solution and semiconductor conditions.

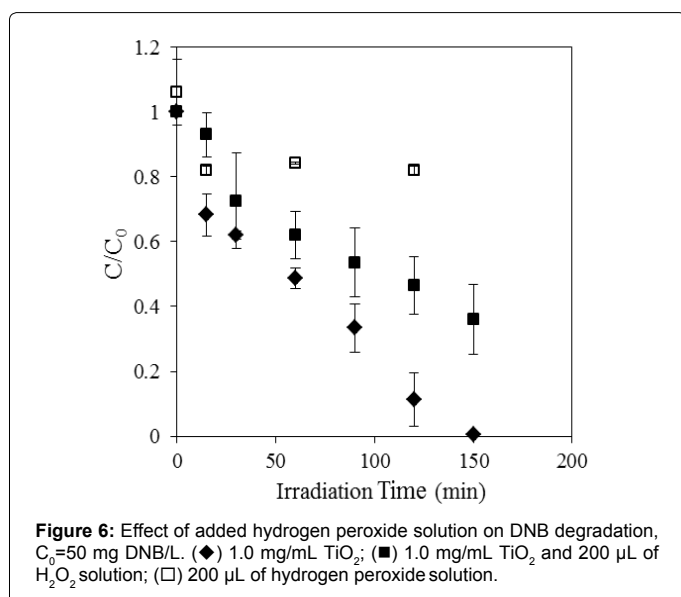
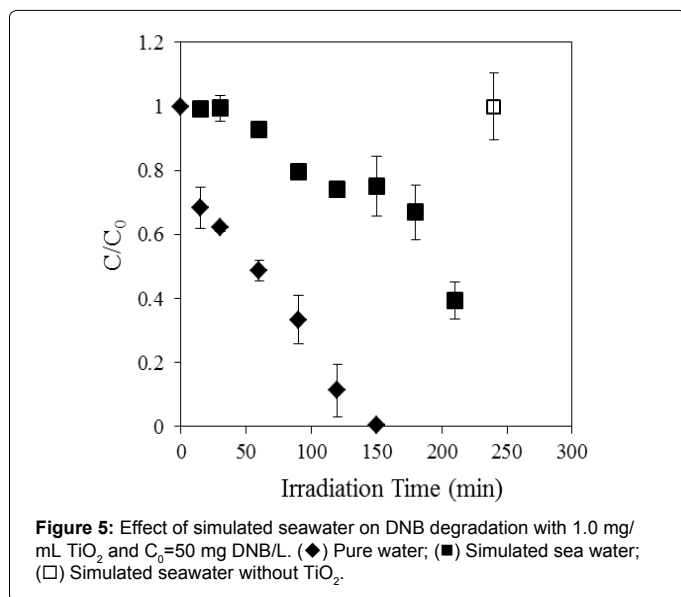


Effect of simulated salt water: Photoreactions performed with DNB solutions prepared using simulated sea water showed a pronounced reduction in degradation rate and only 60% DNB removal was achieved after 150 minutes of irradiation, as seen in Figure 5. The effect of dissolved ions may lower the reactivity of radicals or other charged participants in the reaction. These results again contrast with those of Mihás [12] who observed that the rate of photolysis increased significantly for 2,4 dinitrotoluene solutions in seawater versus groundwater or deionized water.

Effect of additives for potential reaction rate enhancement

Addition of hydrogen peroxide: In addition to understanding the impact of potential environmental contaminants on the rate of heterogeneous photocatalysis, it is also important to pursue possible means to enhance oxidation rates through the intentional addition of reagents. To increase the rate of DNB oxidation, 0.2 mL of 3% hydrogen peroxide solution was added to each photovial before reaction. It was hypothesized that the added hydrogen peroxide would generate hydroxyl radicals during irradiation and increase the rate of DNB degradation. The results shown in Figure 7 indicate that the DNB degradation rate was slower in the presence of added hydrogen peroxide and only 60% DNB removal was achieved after 150 minutes of irradiation. This implies that the generation of oxidizing hydroxyl radicals is not the rate controlling step in DNB degradation.

In a study of trinitrotoluene, Dillert also observed that the addition of hydrogen peroxide to TiO_2 suspensions reduced the initial rate of compound destruction for irradiation by light with wavelengths greater than 320 nm [20]. However, a study by Chen [16] on UV photolysis of 0.1 mM DNB solutions showed that the addition of hydrogen peroxide significantly enhanced the photodegradation rate. These results indicate that similar mechanisms cannot be assumed for photocatalysis and photolysis. Shafei studied the effects of added peroxide on terephthalic acid photocatalysis using TiO_2 and ZnO and observed an enhanced oxidation rate for low peroxide loadings but an inhibitory effect at higher concentrations [21]. At low loadings, peroxide was proposed to act as an electron acceptor and increase production of hydroxyl radicals. The inhibitory effect of higher added peroxide concentrations was attributed to the radical scavenging mechanism presented below which would be driven by the concomitantly higher concentrations of peroxide and hydroxyl radicals [21,22]:



Addition of sodium nitrate: A second test for the impact of hydroxyl radical generating compounds on heterogeneous photocatalysis of DNB was performed using sodium nitrate. The amount of sodium nitrate added to each photovial was calculated to match the estimated yield of hydroxyl radicals by irradiation of the H₂O₂ added to photovials in the hydrogen peroxide experiments [23]. The results in Figure 7 for the addition of NaNO₃ are quite similar to those for the addition of hydrogen peroxide solution shown in Figure 6. In both cases, the addition of a reagent that generates hydroxyl radicals during irradiation slowed the rate of DNB degradation.

Use of acetone cosolvent

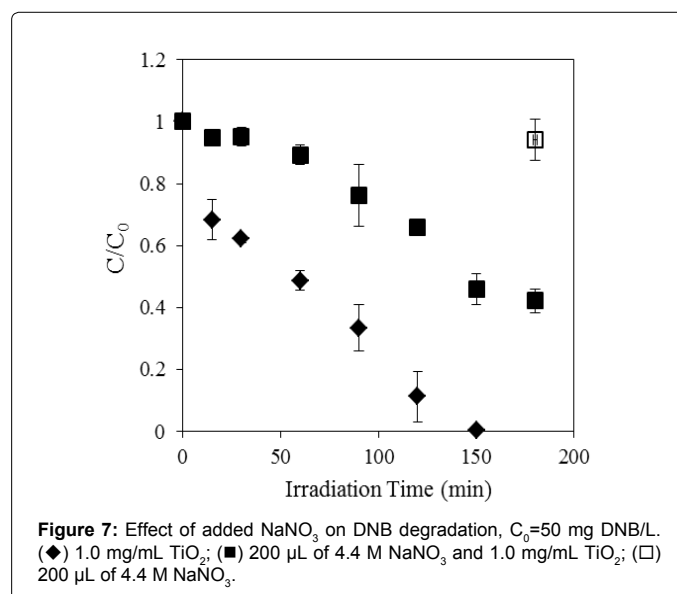
One limitation in applying heterogeneous photocatalysis to remediate contaminated environments is the solubility of the analyte. Although the reported solubility of DNB in water is as high as 0.53 g/L [24], in this work, dissolution of only 50 mg/L into pure water often

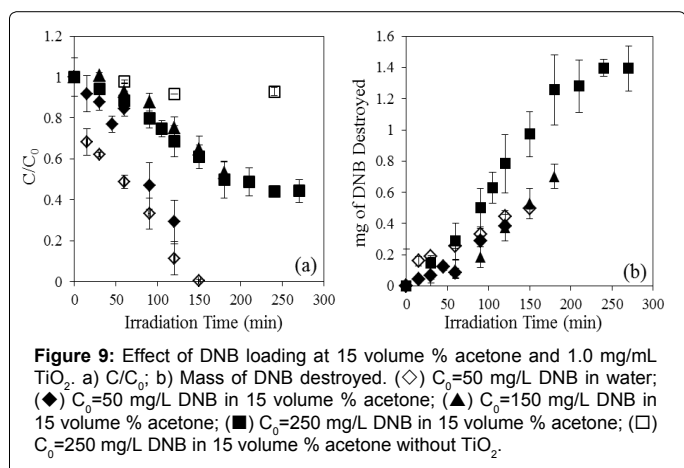
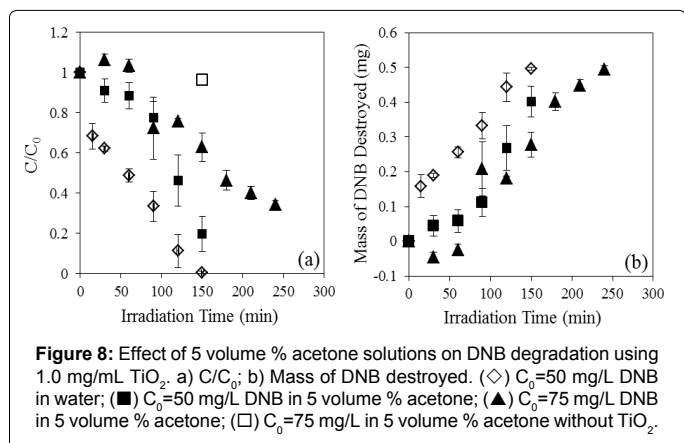
took several hours with the aid of sonication and heating. Leiga also reported lower solubility of DNB in solutions containing NaCl and DNB solubility that was enhanced at low concentrations of sodium p-toluenesulfonate yet significantly reduced at higher concentrations of this salt.

From the sensitivity of DNB solubility to other solutes, it was inferred that dissolution of DNB into a mixed aqueous/organic solution might enable a higher rate of DNB destruction. Methanol, a potential cosolvent for DNB acts as hole scavenger in heterogeneous photocatalysis [25] and was expected to compete with DNB oxidation. Acetone, a good solvent for DNB, was shown to be less reactive in UV heterogeneous photocatalysis [26] and was selected as the cosolvent.

Figure 8 shows results for heterogeneous photocatalysis of 50 mg/L DNB in pure water versus 50 mg/L and 75 mg/L DNB solutions containing 5 volume % acetone. For 50 mg/L solutions, the presence of acetone reduces the DNB degradation rate, which can be attributed to competitive oxidation of acetone. The 75 mg/L DNB solution in 5 volume % acetone shows the smallest relative concentration change, however on a mass basis, this solution degrades the same amount of DNB as the pure water solutions.

Figure 9 shows further experiments were performed with DNB solutions containing 15 volume % acetone to compare the degradation effectiveness for solutions containing 50 mg/L up to 250 mg/L of DNB. The 50 mg/L DNB solution in pure water again gave a faster degradation rate than the same concentration with 15% acetone cosolvent. However the higher concentration solutions made with the acetone cosolvent gave significantly larger mass destructions of DNB and slightly faster degradation rates than what was achieved using pure water. For high DNB loadings at extended times, the mass destruction appears to reach a maximum. It is considered unlikely that this is associated with depletion of dissolved oxygen in the closed reaction system, because the addition of hydroxyl radical generating chemicals did not enhance the DNB degradation rate. For these cases, it is proposed that a more likely cause for reaction termination is adsorption of products or byproducts on the TiO₂ surface or the formation of products with strong light absorption. Although the cosolvent adds further chemicals into the solution, it may be a useful strategy for enhancing the destruction of a high toxicity contaminant.





Conclusions

Heterogeneous photocatalysis is a complex process that can be affected by the characteristics of the analyte and other solutes in solution and the interaction of each species with the TiO₂ surface. The effects of other chemicals potentially present in an aqueous waste stream containing DNB were tested by adding acetic acid, fulvic acid and seawater salts to the solution. Each was shown to inhibit the rate of DNB degradation. The addition of hydroxyl radical generating compounds, including H₂O₂ and sodium nitrate also yielded slower DNB degradation rates. These results were used to infer that for DNB photooxidation under simulated sunlight, hydroxyl radical generation is not the limiting step in the overall mechanism. Use of an acetone cosolvent gave a lower relative rate of DNB degradation yet allowed for the destruction of larger masses of DNB. The use of cosolvents may provide a means to enhance the treatment of low aqueous solubility contaminants released to the environment.

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