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Elsie Kitcher

Stevens Institute of Technology

Washington Braida

Stevens Institute of Technology

Agamemnon Koutsospyros

University of New Haven, akoutsospyros@newhaven.edu

Julius Pavlov

Stevens Institute of Technology

Tsang-Liang Su

Stevens Institute of Technology

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Characteristics and products of the reductive degradation of 3-nitro-1,2,4-triazol-5-one (NTO) and 2,4-dinitroanisole (DNAN) in a Fe-Cu bimetal system

E. Kitcher¹, W. Braidia, Ph.D.¹, A. Koutsospyros, Ph.D.², J. Pavlov, Ph.D.¹, T.-L. Su, Ph.D.^{1*}

1. Center for Environmental Systems, Stevens Institute of Technology, Hoboken, NJ 07030, United States
2. University of New Haven, 300 Boston Post Road, West Haven, CT 06516, United States

*Corresponding author: e-mail: E-mail: t1su@stevens.edu, Tel. 201-216-5697; Fax: 201-216-8303

Abstract

It has been shown previously that, under acidic conditions, 3-nitro-1,2,4-triazol-5-one (NTO) and 2,4-dinitroanisole (DNAN) degrade in the presence of iron/copper bimetal particles; the reactions can be modeled by pseudo-first-order kinetics. This study investigates the reaction mechanisms of the degradation processes under different conditions. Batch studies were conducted using laboratory-prepared solutions and an industrial insensitive-munitions-laden (IMX) wastewater. The influence of parameters such as initial pH of the solution, copper/iron (Fe-Cu) contact and solid/liquid ratio were systematically investigated to assess their impact on the reaction kinetics. These parameters were subsequently incorporated into pseudo-first-order decomposition models for NTO and DNAN. The activation energies for the degradation reactions were 27.40 kJ/mol and 30.57 kJ/mol, respectively. Degradation intermediates and products were identified. A nitro to amino pathway, which ultimately may lead to partial mineralization, is postulated. The amino intermediate, aminonitroanisole, was detected during DNAN degradation, but for NTO, aminotiazolone is suggested. Additionally, urea was identified as a degradation product of NTO.

Keywords: NTO, DNAN, IMX, reductive decomposition, Fe-Cu, bimetallic particles,

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1. Introduction

Munitions that explode only under intended conditions are known as insensitive munitions (IM). They are, for example, shock-insensitive and were developed to minimize accidental detonations. 3-nitro-1,2,4-triazol-5-one (NTO, $C_2H_2N_4O_3$) and 1-methoxy-2,4-dinitrobenzene (2,4-dinitroanisole or DNAN, $C_7H_6N_2O_5$) are typical components of IM formulations such as IMX-101, IMX-104, and PBXW-124 (Figure 1).

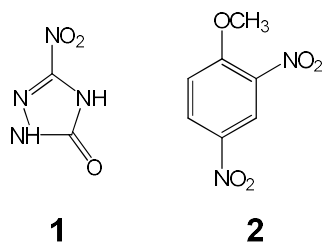


Figure 1. Chemical structures of NTO (1) and DNAN (2).

DNAN and NTO are suitable replacements for the more sensitive 2,4,6-trinitrotoluene (TNT). For example, NTO offers comparable explosive power to hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) but it is less sensitive to heat and mechanical shock. The use of these compounds in munitions formulations necessitates the presence of treatment facilities for wastewater streams. The aquatic solubility of DNAN has been reported to be between 0.276 g/L (Boddu et al 2008) and 0.632 g/L (Koutsospyros et al 2012), and that of NTO as 12.8 g/L (Koutsospyros et al 2012). The release of chemicals with such relatively high solubilities to the environment can cause widespread contamination of soils, sediments, and water bodies due to facile environmental transport. Toxicological information about NTO and DNAN shows that both compounds are potentially toxic to humans and ecosystems (Kennedy et al 2013, Reddy et al 2011, Dodard et al 2013); thus, it is of prime importance to treat such IM-laden wastewaters prior to release to the environment.

Both physicochemical and biological methods have been used for the remediation of munitions-laden streams. Le Campion et al (1999) compared the photocatalytic degradation of NTO with Fenton oxidation at low NTO concentrations. Both methods led to the complete mineralization of NTO. The same group (Le Campion et al 1998) as well as Krzmarzick et al (2015) show that microbial remediation of NTO is via nitro-reduction of the compound, followed by the formation of a primary amine, 5-amino-1,2,4-triazol-3-one (ATO). The end products of the biodegradation were carbon dioxide, urea and a polar compound, which they assumed to be hydroxyurea. During electro-reduction of acidic aqueous solutions of NTO, Cornin et al (2007) identified the intermediate azoxytriazolone (AZTO) instead.

DNAN, however, is transiently converted to both nitroso and hydroxylamine intermediates by aerobic soil bacteria before being reduced to 2-amino-4-nitroanisole (Perreault et al 2011). DNAN severely inhibits methanogens and nitrifying bacteria but is notably less inhibitory to aerobic sludge (Perreault et al 2011). Other studies (Platten III et al 2010; Ahn et al 2011; Olivares et al 2013) have indicated 2-amino-4-nitroanisole (2-ANAN) and 2,4-diaminoanisole (DAAN) as products of biotic or abiotic transformation of DNAN. Recently, Hawari et al (2014) reduced DNAN with zero-valent iron (ZVI) and bacteria under aerobic conditions, and region-selectively produced 2-ANAN and/or DAAN.

Bimetal systems have also been used in the remediation of munitions-laden streams. The system consists of combinations of two metals chosen for their standard reduction potentials - the primary metal having the lower redox potential. The primary and secondary (catalyst) metal form a galvanic cell, which facilitates electron transfer. For example, remediation of wastewaters contaminated with TNT (Fidler et al 2010), RDX (Krzmarzick et al 2015; Koutsospyros et al 2012; Wanaratna et al 2006; Gilbert & Sale 2005) and trichloroethylene (TCE) (Chao et al 2012; Kim & Carraway 2003;

Liang et al 1997) demonstrated that iron-based bimetal systems had much higher reactivity than just zero-valent iron. The nature of the transformation with bimetals suggests sequential but direct surface-mediated reduction pathways which can be modeled by pseudo-first-order kinetics. DNAN and NTO degrade under controlled conditions following pseudo-first-order kinetics in bimetal systems (Fe-Cu and Fe-Ni), as indicated by Koutsospyros et al (2012). The objectives of this study were (a) to conduct a kinetic study of reductive degradation of NTO and DNAN using Fe-Cu bimetals; (b) to investigate parameters affecting reaction rates (pH, oxidation-reduction potential (ORP), temperature, Fe-Cu mass ratios, solid-to-liquid ratio); (c) to identify products and intermediates generated during reductive degradation of NTO and DNAN and (d) to propose a possible reductive pathway for the target compounds.

2. Materials and Methods

2.1. Stock solutions and wastewater

Stock solutions of NTO were prepared from the pure solid (supplied by Picatinny Arsenal, NJ, USA), by dissolving in deionized (DI) water to achieve an average final concentration of 800 mg/L. DNAN (98%, from Sigma-Aldrich) was dissolved in 100 mL acetonitrile, and then diluted with DI water to 8L at an average final concentration of 300 mg/L. The IMX wastewater was supplied by Picatinny Arsenal (NJ, USA). The concentrations of the energetics in the IMX wastewater received from the manufacturing facility varied considerably: 1000 - 1700 mg/L for NTO and 150 - 500 mg/L for DNAN. All the solutions were stored at room temperature (21 ± 1 °C).

2.2. Batch experiments

The zero-valent iron material employed was H200 Plus™ (Hepure Technologies, DE, USA). The average particle size was 70 micron (range 5 – 100 micron), distributed as follows: +60 mesh (>250 micron) – 1% maximum, -100/+325 mesh (45 – 150 micron) report, -325 mesh (<45 micron) 15-

40%. The copper metal employed was 185E (Acupowder International, NJ, USA), average particle size 45 micron. The Fe-Cu mixtures were prepared by mixing the iron and copper powders in 60 mL plastic tubes by vigorous physical shaking for 1 minute. The amount of iron in the mixtures was kept constant in all cases, and only the amount of copper was varied to adjust the Fe-Cu mass ratio. For each Fe-Cu mixture, triplicate bench-scale experiments were performed in vial reactors by adding 0.25 g, 0.50 g or 1.0 g iron particles to 50.0 mL of NTO, DNAN, or IMX solutions to give three different solid to liquid (S/L) ratios of 0.5%, 1%, and 2% of each IM investigated. Also, four ratios of Fe-Cu (2.5:1, 5:1, 10:1, and pure Fe) were prepared and used in separate experiments. (A flow diagram of the experimental procedure and a Table summarizing the experimental parameters for a given substrate solution and initial pH level are presented in the Supplementary Information.) The 60 mL vials with Fe-Cu particles and IM solutions were then tumbled end-over-end at approximately 30 rpm on a rugged rotator (Glas-Col, Terre Haute, IN, USA). At selected time periods during the batch experiments, pH (Accumet® glass Ag/AgCl electrode) and ORP (MW500 ORP Meter, platinum electrode) were measured. Samples were taken and filtered (Whatman Puradisc nylon syringe filters with 13mm diameter; pore size: 0.45 μm ; non-sterile) into 2 mL high-performance liquid chromatography (HPLC) vials containing 20 μL of glacial acetic acid ($\geq 99.7\%$ w/w, Fisher Scientific, Pittsburgh, PA, USA) to keep the dissolved iron from precipitating. The samples were analyzed by HPLC for the target compounds. All reagents were HPLC grade. The experiments were performed at three different initial pH levels: 2.3, 2.9, and 3.3. These values were chosen because, in order for the Fe reduction to proceed, NTO must be mostly in its undissociated state ($\text{pK}_a = 3.5$); at neutral or basic pH levels the reaction does not take place. Brunauer–Emmett–Teller (BET) 5-point analysis was used to estimate the specific surface area of iron; that was found to be 1.65 m^2/g . Acetic acid was used to adjust the initial pH of the solutions to 2.9 and 3.3, but drops of nitric acid (70%, Fisher Chemical) were used, when needed, to adjust the pH to 2.3. Since the focus of this study was industrial-scale applicability, purging the wastewater would not be practical because an increase in

operational costs would supersede the retardation experienced in the reaction rate. These batch experiments were repeated for laboratory-prepared solutions of NTO and DNAN at five different temperatures (15 °C, 20 °C, 25 °C, 30 °C & 35 °C) in a temperature-controlled chamber (Standard Environmental Systems Inc., USA, Model HB/12) at pH 2.3, iron-copper ratio 10:1 with total iron mass 0.15g. The particles were added to the solution after an hour of rotation at the pre-determined temperature (tumbling end-over-end in a rugged rotator at 30 rpm as above).

2.3. Analysis/Instrumentation

All HPLC analyses were performed on a Varian 920 HPLC (Agilent Technologies, CA, USA). For NTO analysis, a Thermo Scientific HypercarbTM (porous graphite) 5 μ m, 4.6 mm \times 150 mm column was used. The eluent was an isocratic mixture of water: [acetonitrile + 0.1% trifluoroacetic acid] 85:15 (v/v), pumped at 1.0 mL/min. The injection volume was 5 μ L. The analytical wavelength was at 316 nm of diode-array detector. NTO eluted at 9.0 minutes under these conditions. For DNAN analysis, a Grace Davison (Alltech) Vydac 218TP C18 Column, 4.6 mm x 250mm, 5 μ m particle size, was used. The eluent was an isocratic mixture methanol: water 60:40 (v/v), pumped at 1.0 mL/min. The analytical wavelength was at 284 nm of diode-array detector and the injection volume was 5 μ L. DNAN eluted at 4.1 min under these conditions. A Waters Micromass Quattro Ultima mass spectrometer (Manchester, UK) equipped with a Z-spray source was used in the electrospray mode to identify of intermediates and decomposition products. The capillary voltage was set at \pm 3.5kV, the cone voltage 10-15V, and the infusion rate was 10-20 μ L/min. Inductively-coupled plasma optical emission spectroscopy (ICP-OES) (Varian Vista MPX, Palo Alto, CA, USA,) was used to measure concentrations of dissolved metals.

3. Results and Discussion

Preliminary batch experiments using Fe-Cu particle mixtures were performed to derive kinetic information. The ORP during the batch experiments decreased by values in the range of 300-400 mV; conversely, pH increased by as much as 2 units. The HPLC results indicated that NTO and DNAN were rapidly degraded in the presence of Fe-Cu bimetals. (See supplementary materials).

3.1. Rate expression and constants

The reductive bimetal-based degradation of IMs is a heterogeneous reaction that occurs for the most part on the active sites of the surfaces of the iron particles. In that case the reaction would follow second order kinetics as described by the following equation:

$$-dc/dt = k_2 C_{Fe} C \quad [1]$$

where C = IM concentration, mol m⁻³,

C_{Fe} = concentration of iron (active sites) mol m⁻³

t = elapsed time, min

k_2 = second-order reaction rate constant, m³ mol⁻¹·min⁻¹

Consequently, the concentration of active sites, C_{Fe} , can be expressed by the following equation:

$$C_{Fe} = k \alpha_s C_M \quad [2]$$

Where C_M = mass concentration of Fe, g m⁻³ of solution

α_s = specific surface area of Fe, m² g⁻¹

k = number of active sites per unit area of Fe; mol m⁻²

Thus, substitution of Eq. 2 into 1 gives:

$$-dc/dt = k_2 k \alpha_s C_M C \quad [3]$$

And combining the two constants of Eq. 3 gives:

$$-dc/dt = k_{SA} \alpha_s C_M C \quad [4]$$

where k_{SA} is the normalized surface area reaction rate constant, m min^{-1}

Under the conditions of the batch experiments (constant solids-to-liquid ratio and constant size distribution of Fe particles), Eq. 4 can be written in terms of the observed rate constant (pseudo-first order expression) which can be readily determined from time concentration profiles obtained from batch data:

$$-dc/dt = k_{obs} C \quad [5]$$

Where k_{obs} = the observed pseudo-first order reaction rate constant, min^{-1}

The average concentration of dissolved iron and copper was 582 mg/L and 8 mg/L, respectively, for all solutions after an hour of tumbling at initial pH 2.3, S/L 1% and 5:2 Fe-Cu. The concentration of the metallic iron in suspension was treated as constant as the total amount of dissolving iron was less than 10% of the initially added. The pseudo-first-order rate constants for each set of conditions were obtained through nonlinear (exponential) regression fit. The pseudo-first-order model fitted well to the experimental data (supplementary material).

Data from ambient-temperature experiments indicated that NTO completely degraded within 15 minutes for S/L ratio of 0.5% and within 10 minutes for S/L ratio of 1%, when the laboratory-prepared solution was used. However, DNAN degraded slower, and its complete removal from the laboratory-prepared was observed at 25 minutes and 15 minutes for S/L ratios 0.5% and 1%, respectively. For the IMX wastewater, the total removal of DNAN and NTO was accomplished within 60 minutes under all investigated conditions. This decrease in the removal rate, as compared

with the laboratory-prepared pure-compound solutions, is likely due to the presence of other compounds in the wastewater which may compete with the target compounds for the active sites on the iron surface. Furthermore, a possible competition between NTO and DNAN themselves for the same active sites would also prolong the overall reaction time. Nevertheless, the observed removal rates were higher compared to those in microbial degradation of same compounds, reported to take at least 2 weeks (Le Campion et al 1998; Krzmarzick et al 2015) or 225 days (IMX-101 constituents) by phytoremediation (Richard & Weidhaas 2014), or 21 days (DNAN) by photolysis as reported by Hawari et al (2014).

The rate constants for 2% S/L ratio experiments could not be determined for the laboratory-prepared because the reaction rates were very high: neither NTO nor DNAN was detected after 2 minutes, when the second sample was taken.

3.2. Activation Energy

Kinetic experiments were conducted at five different temperatures (15 °C, 20 °C, 25 °C, 30 °C & 35 °C) to determine the activation energy (E_a) based on the Arrhenius equation [Eq. 6, Figure 2]:

$$\ln k = \ln A - E_a/RT \quad [6]$$

The activation energies were determined as 27.40 kJ/mol for NTO and 30.57 kJ/mol for DNAN.

These values suggest that the reduction reactions of NTO and DNAN by Fe-Cu particles are surface-controlled reactions. Diffusion-controlled catalysis reactions generally have low activation energies, in the range of 10-16 kJ/mol, while it is characteristic for surface-controlled reactions to have higher activation energies, typically greater than 30 kJ/mol (Su & Puls 1999; Heilmann et al 1996; Pilling & Seakins 1996; Spiro 1989; Laidler 1965).

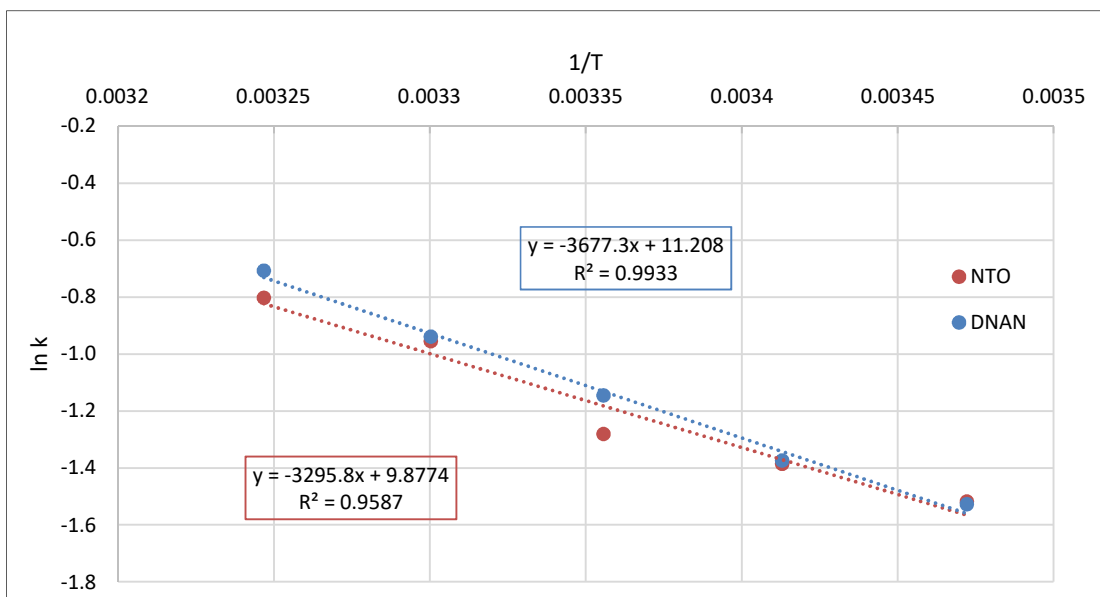


Figure 2. Activation Energy plot for NTO. Arrhenius equation 1/T vs ln k.

3.3. Effect of initial pH on the rates of reactions

In both the laboratory-prepared solution and the IMX wastewater tested, the degradation of NTO and DNAN was the fastest at $\text{pH} \leq 2.9$. Between $\text{pH} 2.9$ and 2.3 (the latter being the lowest attempted), the reaction rates were fairly constant, (k_{obs} not statistically different considering the standard errors – see supplementary material). At lower pH levels, the increased rate of iron dissolution provides for a stronger reducing environment for the destruction of the organic compounds. In the case of NTO lower pH favors the non-dissociated (reactive) form. The iron-to-copper ratios did not significantly influence the reaction for either the laboratory-prepared solutions or the IMX wastewater.

A series of experiments were conducted to determine if the nature of the acid used to decrease the pH affects the reduction process. Two mineral acids (hydrochloric, HCl, and nitric, HNO₃) and two organic acids (acetic, CH₃CO₂H, and formic, HCO₂H) were used for this purpose. Intriguingly, the type of acid used had significant impact on the reaction rates. As shown in Figure 3, the mineral acids considerably lowered the reaction rates compared to the organic acids for all samples (IMX

Figure 3a-b and laboratory-prepared solution Figure 3c-d). The improved performance of the system with organic over mineral acids may be due to the added buffering capacity by the former.

The buffer capacity tends to resist a pH increase which impairs the process by promoting iron corrosion and thus limits available surface active sites.

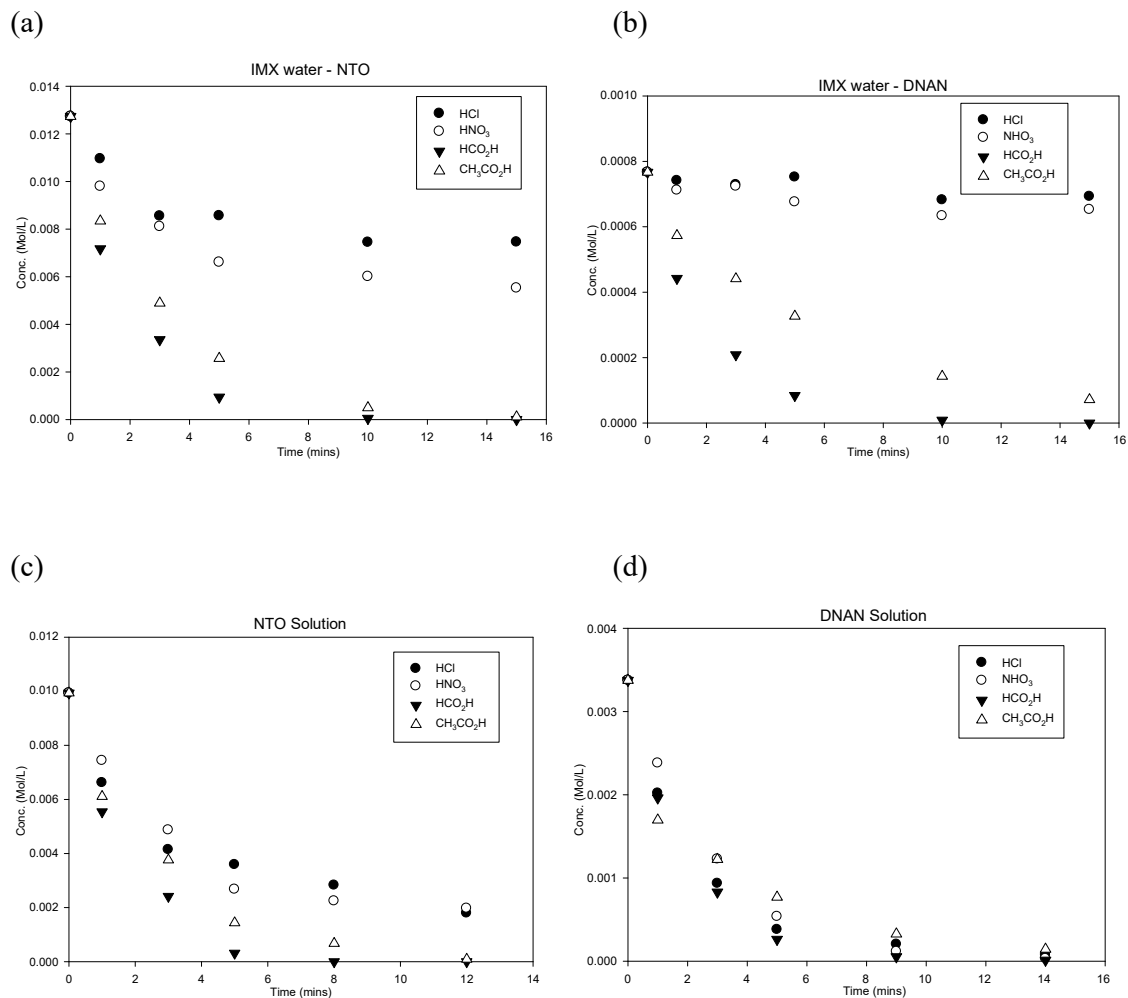


Figure 3. Effect of different acids (Concentration vs Time) on the reduction of (a) NTO in IMX wastewater (b) DNAN in IMX wastewater (c) laboratory-prepared NTO in solution, and (d) laboratory-prepared DNAN in solution.

3.4. Influence of solid (Fe^0) vs dissolved (Fe^{2+}) iron

To establish whether the reaction occurs at the surface of the particles or rather in solution, the following experiments were conducted. One hundred mg/L of $FeSO_4$ was added to the target compound solution and the reaction was observed for 3 minutes. Minimal removal (0-5%) was observed before the addition of the bimetals. In stark contrast, the addition of the bimetals resulted in dramatically increased removal rates in all samples (Figure 4). These results support the hypothesis that the contaminant degradation occurs predominantly via a surface reaction.

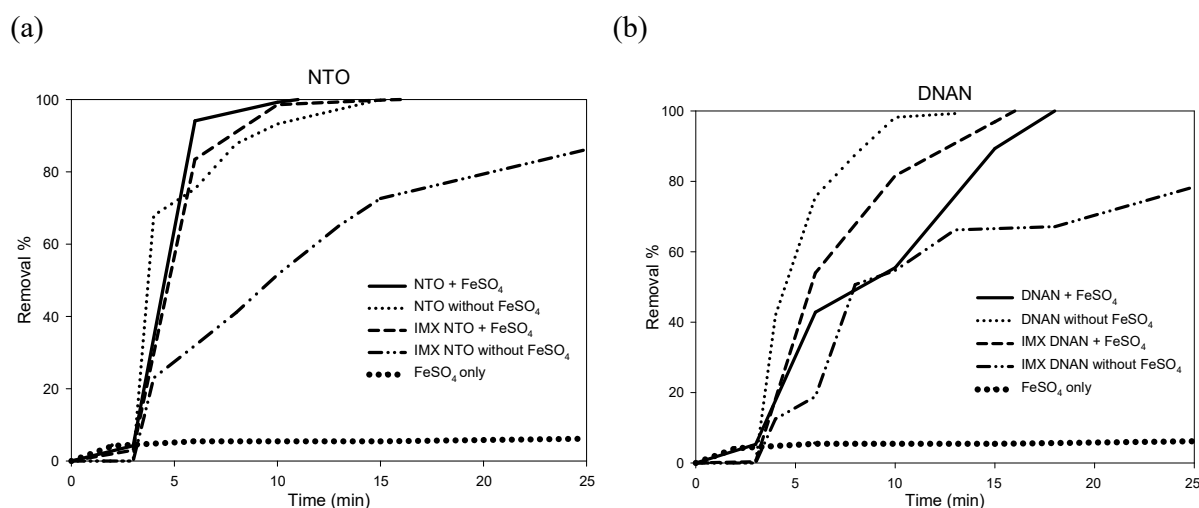


Figure 4. Confirmation of surface-mediated hypothesis for (a) NTO and (b) DNAN in Fe-Cu bimetal system.

Additional evidence for the surface-mediated reaction was provided by an experiment where only copper particles were allowed to react with the compounds of interest. Even though some of the removal (10% and 20% decrease in the concentrations of DNAN and NTO over 24 hours) can be attributed to adsorption onto the copper surface, this is insignificant considering that the reaction time for the degradation of the NTO and DNAN does not exceed 60 minutes.

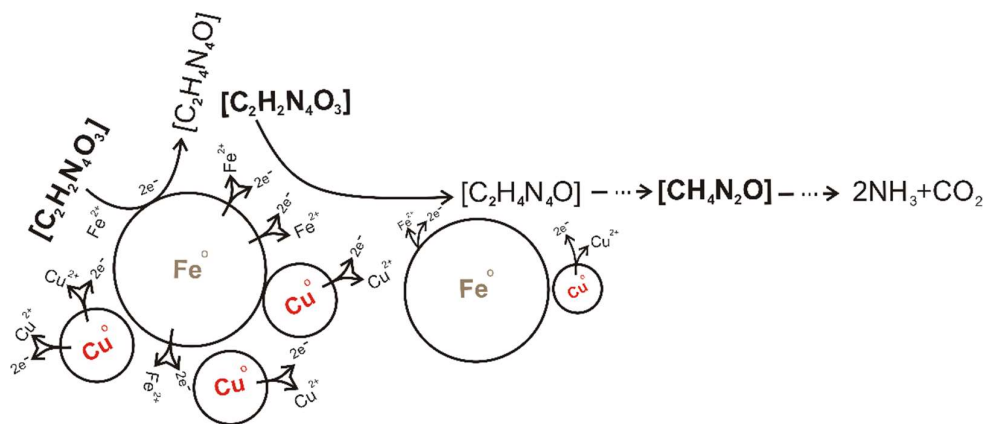


Figure 5. Graphical representation of NTO degradation on a Fe/Cu galvanic cell.

3.5. Type of contact between iron and copper

To further investigate the character of the iron-particle reactive surface, two types of bimetals were prepared for the purposes of comparison. One was a physical mixture of iron and copper particles, while the other was prepared by the cold deposition of copper onto iron via a copper salt solution (chloride or sulfate). The coated particles were more effective at degrading NTO and DNAN (Table 1). The galvanic effect was reduced due to the less-than-optimum physical contact between iron and copper in physically mixed particles (Figure 5), as opposed to the chemical deposition of copper onto iron. The current study opted for mechanical mixing rather than chemical coating because the former approach is faster, easier and cheaper to prepare, therefore making it more feasible and applicable in industrial settings.

Particles	k_{obs} (min^{-1})			
	NTO	IMX NTO	DNAN	IMX DNAN
SO_4^{2-} (5g/L)	0.407	0.541	0.245	0.177
SO_4^{2-} (2.5g/L)	0.329	0.628	0.193	0.201
Cl^- (5g/L)	0.459	0.710	0.320	0.339
Fe-Cu (10:1)	0.425	0.412	0.228	0.289
ZVI	0.410	0.571	0.333	0.223

Table 1: Copper cold-plating results (Pseudo-first-order rate constants)

3.6. Reaction intermediates and end products

Electrospray ionization mass spectrometry (ESI-MS) was employed to detect and identify reaction intermediates and products. Samples taken at different time points from the reaction mixtures were directly infused into the mass spectrometer. DNAN is observed in the negative ionization mode as its radical-anion produced by electron capture ($M^{\cdot-}$, m/z 198) accompanied by an in-source-generated demethylation fragment ($[M-15]^{\cdot-}$, m/z 183). DNAN itself does not yield any species that can be observed in the positive ionization mode. However, a new peak was observed at m/z 169 in the positive ionization mode from samples taken during the degradation process. Upon collision-induced dissociation (CID), the observed species underwent principal neutral losses of 15 Da (methyl-radical loss, m/z 154), 46 Da (NO_2 loss, m/z 123), and 61 Da (CH_3NO_2 loss, m/z 108) (Figure 6).

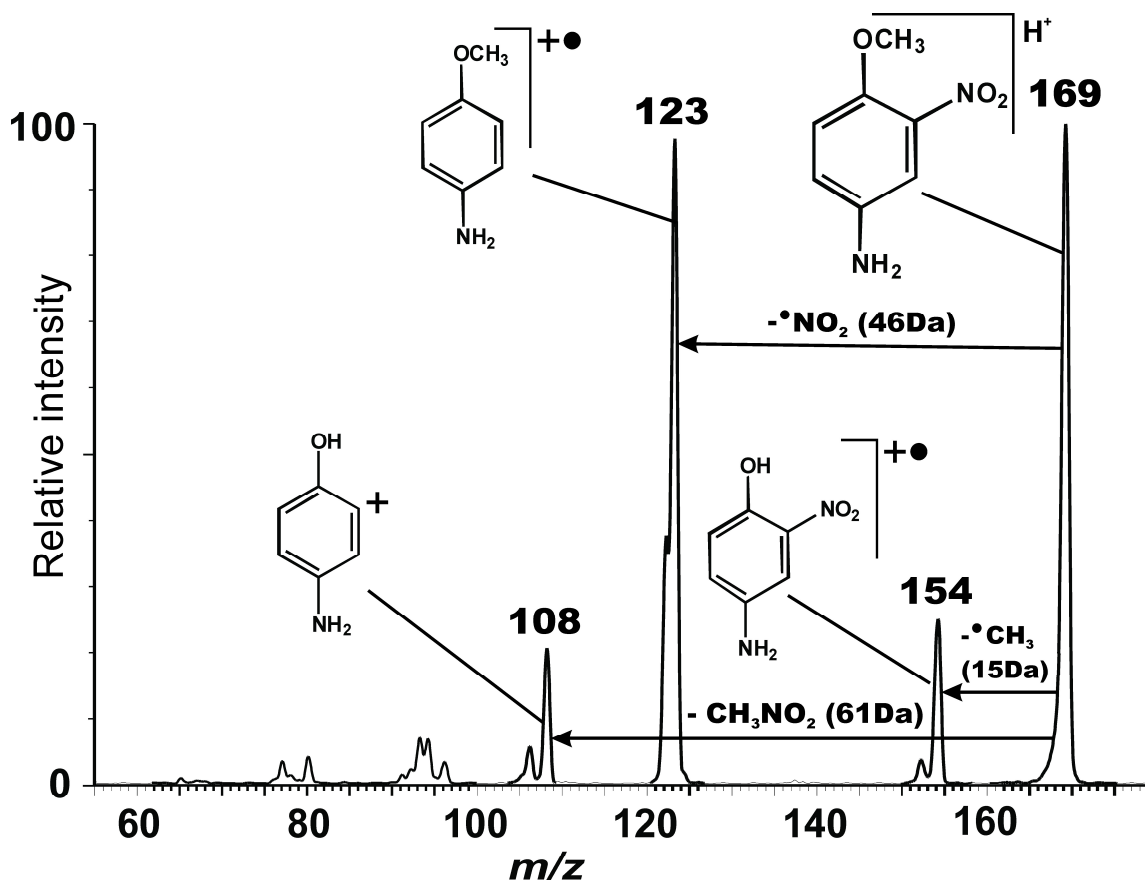


Figure 6. A collision-induced-dissociation mass spectrum recorded from a DNAN reaction intermediate at m/z 169.

Additionally, since the peak at m/z 169 is generated by a protonated species ($[M+H]^+$), the mass difference between the neutral species and that of DNAN is 30 Da. A reduction of one nitro group on DNAN to an amino group would explain the mass difference. An amino group present in the species at m/z 169 was confirmed by an in-source deuterium exchange experiment (Attygalle et al 2014). Upon the introduction of D_2O vapor to the MS ion source, three new peaks at m/z 170, 171, and 172 appeared in addition to that at m/z 169, indicating three exchangeable protons (Figure 7). Since protonation in a molecule with the aforementioned functional groups occurs exclusively on the amino group (Attygalle et al 2014), three D exchanges conclusively indicate the presence of this functional group. It should be noted that unless special circumstances are present, mass spectrometry typically cannot distinguish positional isomers, i.e. it cannot be confirmed which nitro group was reduced, and whether the reduction occurred preferentially at the ortho or para position. It is reasonable to assume that the peak at m/z 169 was generated by both ortho- and para-aminonitroanisole, but only the para-amino species could generate the CID fragment at m/z 108.

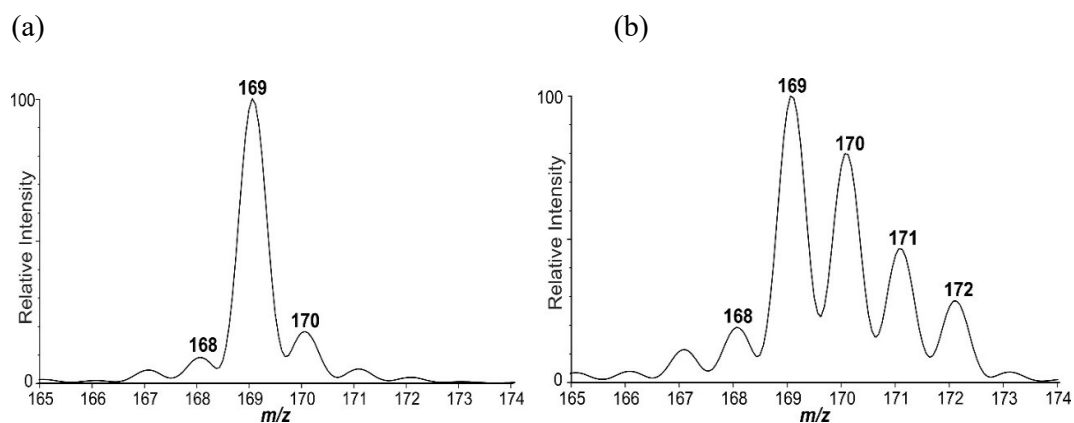


Figure 7. The effect of deuterium exchange on the DNAN reaction intermediate (a) before D_2O was introduced to the source and (b) D_2O exchange at equilibrium.

Intact NTO, being a fairly strong acid (pK_a 3.5), generates a peak at m/z 129 in the negative ionization mode for the deprotonated species ($[M-H]^-$). Even in samples withdrawn after 2 minutes

of Fe-Cu mediated degradation, no MS peak at m/z 129 was observed in the negative mode. Instead, two new peaks were observed in the positive mode at m/z 61 and 121, corresponding to protonated urea and its protonated dimer, respectively. Upon CID, the species at m/z 121 produced a principal fragment at m/z 61 accompanied by a minor one at m/z 103 for a water loss (Figure 8, inset). Samples taken at later stages of the Fe-Cu reduction process of NTO did not generate the urea peaks. Evidently, the degradation of NTO in the Fe-Cu system resulted in complete mineralization. This makes the Fe-Cu bimetal system a more feasible option for the industrial treatment of NTO compared to other approaches (Le Campion et al 1998; 1999; Krzmarzick et al 2015; Chao et al 2012).

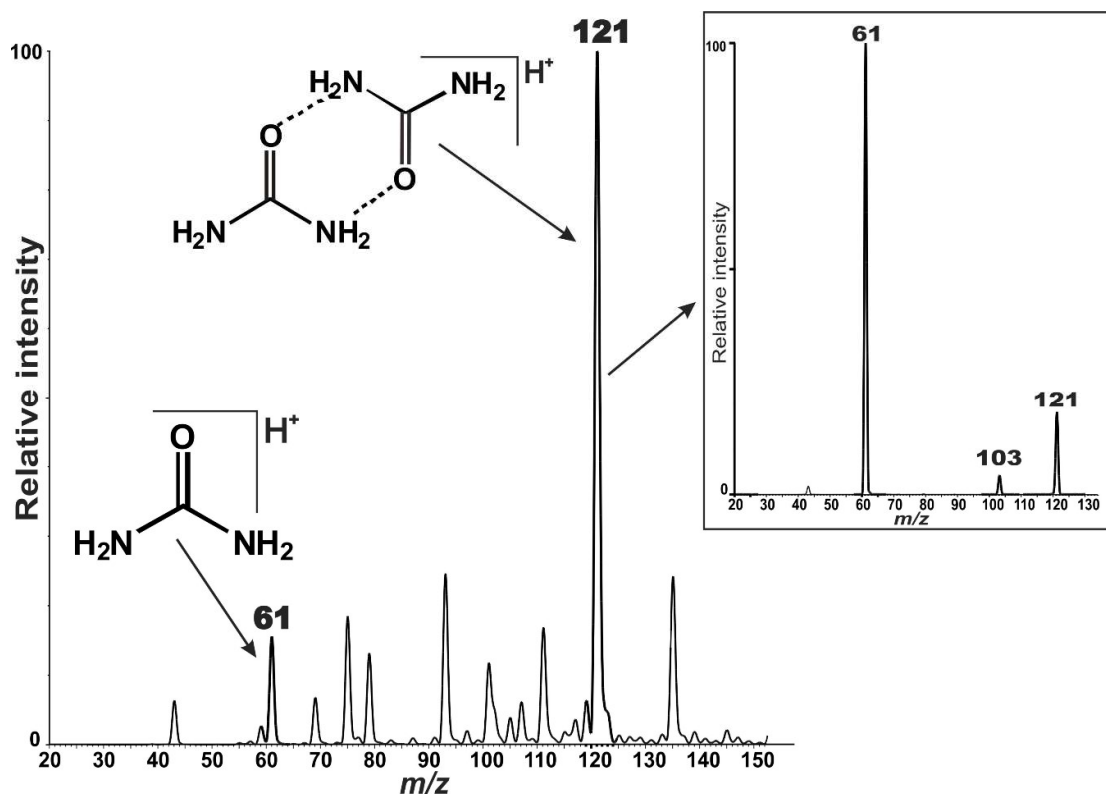


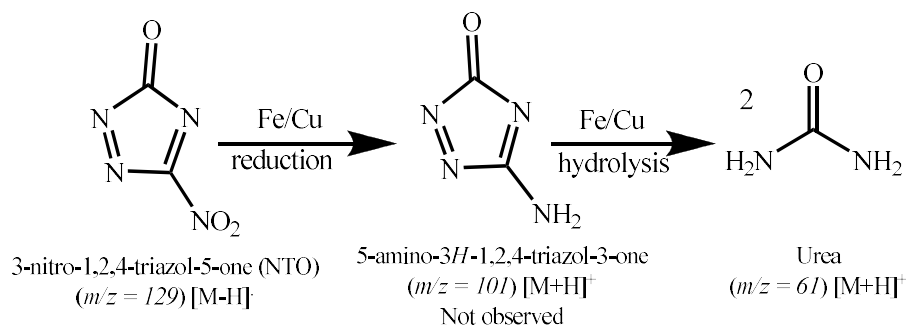
Figure 8. A mass spectrum recorded from an NTO solution at 6 minutes into Fe-Cu degradation.

Insert: CID of the ion at m/z 121.

Thus, no intermediate of NTO degradation was observed, unlike the case of the nitro-to-amino intermediate in DNAN degradation, and this could be due to the high reaction rate of the

transformation. Such an intermediate can, however, be reasonably postulated: its structure would allow two urea molecules to be generated upon dissociation of the original molecule. Figure 9 presents a proposed overall scheme of the degradation pathways for (a) NTO and (b) DNAN.

(a)



(b)

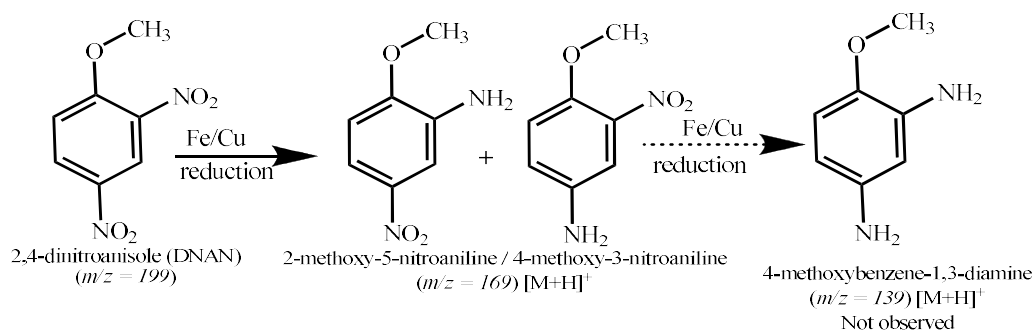


Figure 9. Proposed degradation pathways for (a) NTO, and (b) DNAN in a Fe-Cu bimetal system

As urea does not accumulate in the system, it may have undergone hydrolysis to form NH_3 and CO_2 . This supports the hypothesis of mineralization. Total organic carbon (TOC) measurements that would further corroborate this were not representative under the current experimental conditions, as the solutions were amended with acetic acid. However, there were reductions in total carbon (TC), implying the release of CO_2 gas and some mineralization (data not shown).

4. Conclusion

In this study, the Fe-Cu bimetal system investigated for the remediation of IM-contaminated water effectively degraded NTO and DNAN in laboratory-prepared solutions and in an industrial wastewater. Pseudo-first-order kinetics was used to describe the reductive degradation of NTO and DNAN. The degradation reactions of NTO and DNAN were surface-mediated reactions with activation energies 27.40 kJ/mol and 30.57 kJ/mol, respectively. Lowering the pH increased the rate of the degradation reactions. Organic acids are preferable over mineral acids for decreasing the reaction pH. Experiments verified that the bimetal reduction occurs predominantly at the surface of the iron particles; copper-coated bimetal particles are more effective than physically mixed particles. The reductive degradation of NTO and DNAN proceeds in relatively short time following a nitro-to-amino reduction. In the case of DNAN there is no evidence that the aromatic ring is cleaved. On the other hand, NTO degrades by ring cleavage to yield urea as a final product; since urea does not accumulate, it is possible that the complete mineralization of NTO is attained.

For practical purposes, the short reaction time (efficiency) coupled with the absence of dangerous residual products (effectiveness) at the end of the reaction makes Fe-Cu an attractive choice over other competing methods. In fact, the process is highly amenable to scaling-up, and there are a couple of automated pilot units (500 to 10,000 gpd) currently deployed at US Army facilities. Further studies are currently under way to fully quantify the degradation intermediates and products. Such data would foster further optimization of the reactor design and process for optimal treatment of IM contaminated water at industrial scale, and possibly lead to the elucidation of a generalized kinetic model applicable to industrial design for degradation of similar energetic compounds.

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