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# 1,3-Dinitrobenzene reductive degradation by alkaline ascorbic acid – Reaction mechanisms, degradation pathways and reagent optimization

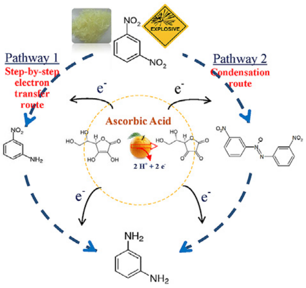
Chiya Ciou, Chenju Liang*

*Department of Environmental Engineering, National Chung Hsing University 250, Kuo-kuang Road, Taichung 402, Taiwan*

## HIGHLIGHTS

- AsA at elevated pH produces electron transfer and governs the electron donating pathway.
- The alkaline AsA reductive reaction is an effective method for the destruction of 1,3-DNB.
- The reduction mechanisms include step-by-step electron transfer and condensation routes.
- Higher NaOH/AsA ratios promote the condensation route and govern the electron release from AsA.
- Eventually, 1,3-DNB was reduced to 1,3-phenylenediamine by the alkaline AsA reductive process.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Nitro-aromatic compounds (NACs) such as 1,3-dinitrobenzene (1,3-DNB) contain the nitrogroup (-$NO_2$), in which the N with a +III oxidation state accepts electrons. Water soluble ascorbic acid (AsA) at elevated pH produces electron transfer and governs the electron-donating pathway. The influence of the NaOH/AsA molar ratio on the degradation of 1,3-DNB was investigated. Using 0.21–2 M NaOH and 20–100 mM AsA, nearly complete 1,3-DNB removals (90–100%) were achieved within 0.5 h. On the basis of intermediates identified using GC/MS, the reduction pathways of 1,3-DNB can be categorized into step-by-step electron transfer, and condensation routes. A higher NaOH/AsA molar ratio would result in relatively higher AsA decomposition, promote the condensation route into the formation of azo- and azoxy-compounds, and ultimately reduce 1,3-DNB to 1,3-phenylenediamine. Contaminated soil flushing using 500 mM NaOH/100 mM AsA revealed that 1,3-DNB was completely degraded within 2 h. Based on these test results, the alkaline AsA treatment method is a potential remediation process for NACs contaminated soils.

## 1. Introduction

Subsurface soil and groundwater contamination by nitro-aromatic compounds (NACs), which consist of at least one nitro group (-$NO_2$) attached to an aromatic ring, is an environmental and

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* Corresponding author.
*E-mail address:* cliang@nchu.edu.tw (C. Liang).

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public health concern because of the acute toxicity of NACs. Many are probable or known carcinogens (Ju and Parales, 2010). NACs have a nitro group and the nitrogen atom, with an oxidation state of (+III) readily accepts electrons, and this has led to the use of NACs in high-energy explosives. Additionally, they are commonly used as starting materials in consumer products such as pharmaceuticals, herbicides, insecticides, solvents and chemical intermediates (Ju and Parales, 2010). 1,3-dinitrobenzene ($C_6H_4N_2O_4$, 1,3-DNB) is a synthetic substance that is used in the manufacture of explosives, and also as an industrial solvent for producing perfumes and drugs (Klein, 2014). Exposure to 1,3-DNB is associated with several health problems including anemia, headache, nausea, and dizziness (ASTDR, 1995). Currently, there are several treatment methods available that are typically recommended for the remediation of NAC contaminated media. Conventional absorption can remove 1,3-DNB from aqueous solution, but this method transfers the 1,3-DNB from aqueous to solid media, and additional technologies (Parham and Saeed, 2014; Zhang et al., 2011) may be required for complete destruction. Microbial degradation can break down pollutants in soil and/or groundwater, but the degradation rate is usually dependent on the environmental conditions (Khan et al., 2015; Smith et al., 2015).

Due to the strong electronegativity of the nitro group, 1,3-DNB can be degraded through reductive pathways by gaining electrons. The use of zero valent iron (ZVI), which exhibits a strong tendency to donate electrons, has been a proven method for reductive degradation of NACs (Sun et al., 2014; Yin et al., 2015). However, due to the solid nature of ZVI in water, its application can cause problems such as: clogging of groundwater flow paths in subsurface remediation applications due to iron precipitation resulting from oxygen or elevated pH in porous media; or the generation of iron sludge in wastewater treatment; or limitation of the mass transfer of dissolved target compounds from the aqueous phase to ZVI surfaces in the ZVI-water system. Ascorbic acid ($C_6H_8O_6$, AsA) (Vitamin C), is a water soluble vitamin commonly present in fruits and vegetables. AsA is a dibasic acid with the dissociation constants $pK_{a1}$ of 4.25 (Eq. (1)) and $pK_{a2}$ of 11.79 (Eq. (2)). Dissolved AsA at elevated pH > $pK_{a2}$ may lose one electron via Eqs. (3) and (4) sequentially, or lose two electrons promptly and then form dehydroascorbic acid ($C_6H_6O_6$, DHA), a stable oxidized form of AsA (Lin and Liang, 2013). Alkaline AsA has been demonstrated to be capable of degrading carbon tetrachloride via dichloroelimination (two-electron transfer) and hydrogenolysis (a sequential one electron transfer) processes (Lin and Liang, 2013). Furthermore, maintaining a high alkaline condition is crucial for producing electron transfer from AsA and governing the electron-donating pathway. Also, an elevated pH condition (e.g., 2 M sodium hydroxide) would favor a two electron transfer mechanism. Threonic acid and oxalic acid were identified as the major AsA decomposition products in alkaline solutions (Liang et al., 2016; Lin and Liang, 2015). It should be noted that 1 mol of AsA upon complete dissociation in accordance with Eqs. (1) and (2) could produce 2 mol of $H^+$, which would neutralize an alkaline pH solution. Lower pH (e.g., < $pK_{a2,\ AsA}$) may reduce electron releases from AsA. Therefore, an alkaline pH buffer or excess hydroxyl ions can maintain the desired pH condition in an AsA solution.

$$C_6H_8O_6 \xrightarrow{pK_{a1}=4.25} C_6H_7O_6^- + H^+ \quad (1)$$

$$C_6H_7O_6^- \xrightarrow{pK_{a2}=11.79} C_6H_6O_6^{2-} + H^+ \quad (2)$$

$$C_6H_6O_6^{2-} \rightarrow C_6H_6O_6^{\bullet-} + e^- \quad (3)$$

$$C_6H_6O_6^{\bullet-} \rightarrow C_6H_6O_6 + e^- \quad (4)$$

$$C_6H_6O_6^{2-} \rightarrow C_6H_6O_6 + 2e^- \quad (5)$$

AsA is a newly developed in situ chemical reduction (ISCR) reagent for soil and groundwater remediation. Our earlier study evaluated the effectiveness of AsA in breaking down the simplest of the NACs, i.e., nitrobenzene (NB), which has one $-NO_2$ functional group (Liang et al., 2016). This study further investigated the ability of AsA to degrade 1,3-DNB, a NB compound containing two $-NO_2$ functional groups. The objectives of this study were to examine the reaction mechanism when using AsA to degrade 1,3-DNB, and to determine the influence of various ratios of NaOH/AsA. A reductive degradation pathway for 1,3-DNB in alkaline AsA solution was proposed. A 1,3-DNB contaminated soil flushing test using alkaline AsA solution was also conducted to evaluate the potential performance of this application as an environmental remediation process.

## 2. Materials and analytical methods

### 2.1. Chemicals

L-Ascorbic acid ($C_6H_8O_6$, 99%), sodium hydroxide (NaOH, ≧99%) and 1,3-dinitrobenzene ($C_6H_4N_2O_4$, 97%) were purchased from Sigma-Aldrich. 3-nitroaniline ($C_6H_6N_2O_2$, 98%) was purchased from Alfa Aesar. Acetonitrile ($CH_3CN$, ≧99%) and dichloromethane (DCM) ($CH_2Cl_2$, ≧99.9%) were purchased from ECHO Chemical. Acetone ($C_3H_6O$) was purchased from J.T.Baker. Water was purified using a reverse osmosis (RO) purification system.

### 2.2. Experiments

The experiments conducted in this study included aqueous and soil phases. In the first aqueous phase experiments, a 2 mM 1,3-DNB solution was prepared by adding pure 1,3-DNB in water and stirred for 24 h to ensure complete dissolution. In a batch aqueous system, to investigate the effects of different experimental conditions, a 7.5 ml solution of either AsA or NaOH was added into 7.5 ml of 1,3-DNB solution in a series of 20 ml amber screw top PTFE/silicone septum glass bottles. In the first part of the experiment, the effect of AsA concentrations (20, 50, and 100 mM) under a fixed NaOH concentration of 210 mM to maintain pH > $pK_{a2}$ (pH = 11.79) was conducted. Assuming that 100 mM of AsA react completely, 200 mM NaOH are neutralized and the remaining 10 mM NaOH would maintain a pH near 12. In the second part of the experiment, the effect of NaOH concentrations (0.5, 1, and 2 M) under a fixed AsA concentration of 100 mM was examined. These batch experiments were conducted in a temperature controlled chamber at 20 °C.

In the second soil phase experiment, 1,3-DNB contaminated soils (sieved through US Sieve #30 (0.595 mm) and retained on US Sieve #200 (0.074 mm)) collected from approximately 2 m below the ground surface, from farm land in southern Taiwan, were prepared by adding 1,3-DNB/acetone solution to the dry soil and then mixing using a reciprocating shaker at 250 rpm for 24 h. Note that the soil used consisted of 97.6% sand and 2.4% clay/silt. The results of a partial characterization of the soil are reported in Table S1 (Supporting Information, SI). Thereafter, the spiked soils were placed on a stainless plate under a fume hood to evaporate the acetone for 1 d at ambient temperature (~25 °C). The resulting soil was stored in a desiccator prior to usage. Testing indicated that the 1,3-DNB concentration was 372 ± 16 mg $kg^{-1}$ (n = 3, error range representing one standard deviation). The preliminary soil flushing experiments were conducted by leaching 60 ml of water,