

1,3-Dinitrobenzene Reductive Degradation by Alkaline Ascorbic Acid: Reaction Mechanisms, Degradation Pathways, and Reagent Optimization

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Background/Objectives. Subsurface soil and groundwater contamination by nitro-aromatic compounds (NACs), which consist of at least one nitro group ($-\text{NO}_2$) attached to an aromatic ring, is an environmental and public health concern. 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. 1,3-dinitrobenzene ($\text{C}_6\text{H}_4\text{N}_2\text{O}_4$, 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. Due to the strong electronegativity of the nitro group, 1,3-DNB containing two $-\text{NO}_2$ functional groups can be degraded through reductive pathways by gaining electrons. Water-soluble ascorbic acid (AsA) at elevated pH produces electron transfer and governs the electron-donating pathway. AsA is a newly developed in situ chemical reduction (ISCR) reagent for soil and groundwater remediation. 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.

Approach/Activities. Laboratory-scale experiments conducted in this study included aqueous and soil phases. In the first aqueous phase experiments, the effect of AsA concentrations under a fixed NaOH concentration to maintain $\text{pH} > \text{pK}_a2$ ($\text{pH} = 11.79$) was conducted and also the effect of NaOH concentrations under a fixed AsA concentration was examined. In the second soil phase experiment, the soil flushings were conducted by leaching water, NaOH, AsA and AsA/NaOH solutions, respectively, into each of a series of open cylindrical funnels, which were filled with 1,3-DNB contaminated soils.

Results/Lessons Learned. This work determined that the alkaline AsA reductive reaction is an effective method for the destruction of 1,3-DNB in aqueous solutions and soils. The rapid 1,3-DNB removal, i.e., 90-100% within 0.5 h when using 0.21-2 M NaOH and 20-100 mM AsA, is attributed to one or two electron transfer steps. The byproducts of 1,3-DNB were identified by the GC/MS analysis and the mechanisms behind the alkaline AsA degradation of 1,3-DNB were proposed schematically in light of the degradation products observed. The reduction mechanisms can be categorized into two pathways: (1) a step-by-step electron transfer route where two nitro groups transformed into nitroso, hydroxylamine, and amine sequentially and (2) a condensation route where nitroso and hydroxylamine groups condensed to azoxy- and azo-compounds. Eventually, 1,3-DNB was reduced to 1,3-phenylenediamine. Moreover, evaluation of the flushing of 1,3-DNB contaminated soils using water, AsA, or NaOH solutions revealed that 1,3-DNB mainly partitioned into the aqueous phase. While using alkaline AsA solutions, 1,3-DNB was completely degraded in both aqueous and soil phases. This study demonstrated that Alkaline AsA can be an effective ISCR reagent. Alkaline pH must be maintained at above a pK_a value of 11.79 during the course of reaction in order to effectively induce releases of electrons from AsA. The results reported here demonstrated that the alkaline AsA reductive process is an effective approach for the treatment of 1,3-DNB contaminated soils.