

Synthesis of benzaldoxime from benzaldehyde using nanoscale zero-valent iron and dissolved nitrate or nitrite



Macharla Arun Kumar^a, Jong Kwon Choe^b, Woojin Lee^c, Sukhwan Yoon^{a,*}

^a Department of Civil and Environmental Engineering, KAIST, Daejeon, 34141, South Korea

^b Department of Civil and Environmental Engineering, Seoul National University, Seoul, 08826, South Korea

^c School of Environmental Science and Engineering, Pohang University of Science and Technology, Pohang, 37673, South Korea

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ABSTRACT

Surface and ground water contamination with $\text{NO}_2^-/\text{NO}_3^-$ is one of the most serious environmental issues due to their adverse effects on human health and ecosystem. Various technologies have been investigated for removal of $\text{NO}_2^-/\text{NO}_3^-$ from surface and ground water; nevertheless, the idea of utilizing $\text{NO}_2^-/\text{NO}_3^-$ contaminated water and wastewater to produce value-added products has not yet been much explored to date. Here, we have developed a novel method for utilizing $\text{NO}_2^-/\text{NO}_3^-$ -contaminated water as a source of nitrogen for the synthesis of benzaldoxime from benzaldehyde using ecofriendly nanoscale zero-valent iron (nZVI) as the reductant. Control experiments with NH_4^+ and NH_2OH supported the proposed reaction mechanism that NH_2OH was generated *in situ* as a reactive intermediate from $\text{NO}_2^-/\text{NO}_3^-$ reduction and reacted with benzaldehyde to form benzaldoxime. The benzaldoxime yield was the largest at the highest temperature tested, 100 °C, and an nZVI-to-N ratio of ~ 7 was optimal for benzaldoxime synthesis. At 100 °C, O_2 in the headspace did not have any negative effect on the reaction. Benzaldoxime yields up to 0.70 ± 0.04 mmol and 0.67 ± 0.05 mmol were observed from reaction of 1 mmol benzaldehyde with 2 mmol NO_2^- and NO_3^- , respectively. Meanwhile, $> 95\%$ of $\text{NO}_2^-/\text{NO}_3^-$ were reduced to either benzaldoxime or NH_4^+ . This novel method suggests a promising option for utilization of water contaminated with $\text{NO}_2^-/\text{NO}_3^-$ for the production of a value-added product.

1. Introduction

Recently, incidents of surface and groundwater contamination with nitrite (NO_2^-) or nitrate (NO_3^-) are becoming increasingly frequent due to various anthropogenic causes, e.g., intensive use of fertilizer in agriculture, discharge of poorly treated industrial wastewater, and massive release of waste from animal feeding operations (Lagerstedt et al., 1994; Scanlon et al., 2007; Wakida and Lerner, 2005). $\text{NO}_2^-/\text{NO}_3^-$ contamination of freshwater systems poses serious threats to human health, disrupt ecosystems and biogeochemical cycles, and diminish sources of safe drinking water (Knobloch et al., 2000). Various remediation techniques have been developed to remove $\text{NO}_2^-/\text{NO}_3^-$ from contaminated waters (Bergquist et al., 2016; Kapoor and Viraraghavan, 1997). Catalytic $\text{NO}_2^-/\text{NO}_3^-$ reduction using supported bimetals with H_2 gas as a reducing agent is a promising technique for the reduction of $\text{NO}_2^-/\text{NO}_3^-$ to N_2 but formation and retention of NH_4^+ still remains an issue (Ding et al., 2017; Hamid et al., 2016; Hamid et al., 2017; Soares et al., 2015). Recently, there is a great interest in recovering energy and resource from treatment of waste and

wastewater; however, the utilization of $\text{NO}_2^-/\text{NO}_3^-$ contaminated water as a potential source of nitrogen for syntheses of value-added organic nitrogen-containing compounds has not yet been explored.

Oximes, nitrogenous organic compounds with general formula $\text{R}^1\text{R}^2\text{C}=\text{NOH}$, are valuable chemicals with diverse utility. Oximes are used as anti-skinning agents, anti-inflammatory agents, antibiotics and anti-oxidants (Chaudhuri, 2003; Ley and Bertram, 2002; Robertson et al., 1995; Tanase et al., 2003), and also as synthetic tools for chemical industry, as they can be dehydrated to nitriles, reduced to amines or transformed to amides via acid-catalyzed Beckmann rearrangement (Crochet and Cadierno, 2015; Henke et al., 2012; Yamaguchi et al., 2007). Due to the high versatility of oximes for both industrial and medical purposes, development of novel and sustainable methods for the synthesis of oximes has recently garnered broad interests (Hyodo et al., 2016). Traditionally, oximes are synthesized by reacting carbonyl compounds with hydroxylamine hydrochloride in presence of stoichiometric amounts of bases (Vogel, 1996). Despite its high reactivity, use of hydroxylamine (NH_2OH) in large-scale industrial processes is not desirable due to its instability and intrinsic toxicity (Gross and Smith,

* Corresponding author.

E-mail address: syoon80@kaist.ac.kr (S. Yoon).

1985). Thus, *in situ* syntheses of NH_2OH from more stable and safe chemical compounds have attracted immense interests from chemists and chemical engineers alike (Pozzo et al., 2002; Raja et al., 2001; Rozner and Neumann, 2006). Oxidation of ammonia with dioxygen or hydrogen peroxide using titanium silicates or polyoxometalates as the catalyst has been suggested as one possible strategy (Pozzo et al., 2002; Raja et al., 2001; Rozner and Neumann, 2006). Until now, only oxidative reaction pathways have been considered for synthesis of NH_2OH , limiting the source of nitrogen to ammonium. Utilization of *in situ* generated NH_2OH from reduction of $\text{NO}_2^-/\text{NO}_3^-$ in contaminated groundwater as the nitrogen source, if possible, would contribute to development of a safe and cost-effective method for oxime production that has an additional benefit of $\text{NO}_2^-/\text{NO}_3^-$ removal from contaminated groundwater.

Nanoscale zero-valent iron (nZVI) is widely known as an ecofriendly material with a large surface area-to-mass ratio and high reactivity (Lu et al., 2016). Magnetic property of nZVI enables effortless separation and recovery of the nanoparticle after its use (Lu et al., 2016). Because of these beneficial properties, nZVI has been broadly used as an effective remediating agent for removal or reductive transformation of a wide range of contaminants in surface water and groundwater (Lu et al., 2016). Effective reduction of $\text{NO}_2^-/\text{NO}_3^-$ using nZVI as a reductant has been previously reported, and recent efforts have been made to enhance its reactivity by adding other metals such as Cu and Pd (Khalil et al., 2016; Ryu et al., 2011; Zhang et al., 2010). Recently, nZVI has also gained attention as a cheap environmentally-friendly catalyst for syntheses of valuable organic chemicals at industrial scale (Hudson et al., 2012; Hudson et al., 2013; Welther and Wangelin, 2013). In this study, we investigated the feasibility of a novel chemical reaction pathway for production of a value-added product benzaldoxime from benzaldehyde utilizing dissolved $\text{NO}_2^-/\text{NO}_3^-$ as the nitrogen source and nZVI as the reductant (Scheme 1), which we expect to further develop into environmental technology for resource recovery from $\text{NO}_2^-/\text{NO}_3^-$ -contaminated waters in the future. No study has reported the synthesis of benzaldoxime from $\text{NO}_2^-/\text{NO}_3^-$ as a nitrogen source or utilization of in contaminated water or wastewater for resource recovery. Specific objectives of this study are to 1) demonstrate the production of benzaldoxime from reduction of $\text{NO}_2^-/\text{NO}_3^-$ coupled with nZVI oxidation in presence of benzaldehyde, 2) identify important reaction pathways that lead to benzaldoxime production, and 3) evaluate the effects of reaction temperature, reaction atmosphere, and the mass ratio of nZVI to N source on the yield of benzaldoxime.

2. Materials and methods

2.1. Chemicals

Ferric chloride (FeCl_3 , > 97%), sodium borohydride (NaBH_4 , $\geq 98\%$), sodium nitrate (NaNO_3 , $\geq 99\%$), sodium nitrite (NaNO_2 ,

$\geq 99\%$), hydroxylamine (NH_2OH) solution (50 wt.% in water) and benzaldehyde ($\geq 99.5\%$) were purchased from Sigma-Aldrich (St. Louis, MO). Ammonium chloride (NH_4Cl , $\geq 99\%$), ethyl acetate ($\geq 99\%$), hexane ($\geq 98.5\%$) and acetonitrile ($\geq 99.9\%$) were obtained from Samchun Pure Chemical Co. (Seoul, Korea). Deaerated deionized water (DDIW) was prepared by purging deionized water (> 18 m Ω cm) with N_2 gas (> 99.999%, Choong-Ang Industrial Gas, Seoul, Korea) for 4 h and stored in an anaerobic chamber (Coy Laboratory Products Inc., Grass Lake, MI) filled with 95% N_2 and 5% H_2 until use.

2.2. Synthesis of nanoscale zero-valent iron

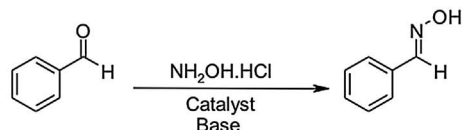
The nZVI particles used in this study were synthesized using a modified version of an established protocol (He and Zhao, 2007). FeCl_3 (14.5 g, 90 mmoles) was dissolved in 100 mL DDIW in a 250-mL Schlenk flask equipped with tunable mechanical stirrer and connected to a N_2 gas supply line. The solution was mixed by stirring at 250 rpm while the headspace was continuously flushed with N_2 . NaBH_4 (13 g, 344 mmoles) was dissolved in 100 mL DDIW and then added to the FeCl_3 solution with a peristaltic pump at a constant flow rate of 10 mL min^{-1} . The mixture was stirred for 30 min, the time length regarded as the end point of hydrogen gas generation (He and Zhao, 2007). The resulting black precipitate was vacuum-filtered through a 0.2- μm PTFE membrane filter (Advantec, Tokyo, Japan) in the anaerobic chamber and the filter retentate was washed with DDIW three times to remove residual dissolved chemicals. The washed filter retentate (wet nZVI) was freeze-dried at -81°C for 24 h and stored in the anaerobic chamber until use.

2.3. Characterization of nZVI

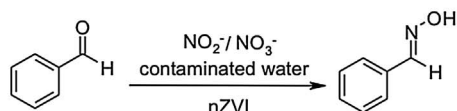
The morphology of synthesized nZVI was observed with a JEM-3010 transmission electron microscopy (TEM) (JEOL, Peabody, MA). The nZVI suspension was diluted with ethanol and sonicated for 10 min to disperse aggregated particles. Several drops of the diluted sample were dropped onto a 300-mesh gold TEM grid with a carbon film. The grid was dried in the anaerobic chamber for one hour before it was analyzed with TEM at 200 kV. X-ray diffraction (XRD) analysis was conducted to identify the crystallinity of nZVI using a D/MAX-2500 automated diffractometer with Cu-KN radiation (Rigaku, Tokyo, Japan). Samples were scanned between 2° and 80° (2θ) with a scan speed of 2°min^{-1} .

X-ray photoelectron spectroscopy (XPS) analysis was performed with Sigma Probe[®] (Thermo Scientific, Waltham, MA) to investigate the oxidation states of Fe on the nZVI surface. The nZVI suspension was carefully transferred to an XPS sampling template in an anaerobic chamber to protect the catalyst surface from exposure to oxygen. The samples were transported to the XPS facility in a gas-tight container with degassed ethanol. The C 1s peak at 285 eV was used as a reference to adjust the results for surface charge effects.

Conventional method using hydroxylamine as the nitrogen source



The method proposed in this study using $\text{NO}_2^-/\text{NO}_3^-$ -contaminated water as the nitrogen source



Scheme 1. Synthesis of benzaldoxime.

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