Reduction of N-Nitrosodimethylamine with zero-valent zinc

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ABSTRACT

N-Nitrosodimethylamine (NDMA) is known as the disinfection by-product and the pollutant in the source water. Reduction with zero-valent zinc (Zn(0)) was investigated as a potential technology to treat NDMA. The results showed that Zn(0) was effective for NDMA reduction at initial pH 7.0. There were lag period and rapid period during the process, the corresponding zero-order rate constant (k_{zero}) was 2.968 ± 0.245 µg L^{-1} h^{-1} ($[Zn(0)]_0 = 10$g L^{-1}),the mass normalized pseudo-first-order rate (k_M) was 0.1215 ± 0.0171 L g^{-1} h^{-1}. The reactivity of zinc on NDMA removal was consistent with the zinc corrosion rate. NDMA had little effect on the corrosion of zinc. Lower solution pH benefited the reduction of NDMA with Zn(0). The consumption of the oxygen and the localized acidification should be the cause of the shift from lag to rapid reaction period in the aerobic experiments. 1,1-dimethylhydrazine (unsymmetrical dimethylhydrazine, UDMH), dimethylamine (DMA) were detected as the products of NDMA degradation. The nitrogen mass balance at 24 h was 56%, the loss can be due to the formation of ammonium, the degradation of UDMH and other unmeasured products. DMA formed during the degradation of UDMH with Zn(0), the nitrogen loss could be caused by the formation of unmeasured products. Catalytic hydrogenation is proposed to be the mechanism based on the results and the redox properties of zinc and NDMA. One reduction process is: the active hydrogen atoms initially cleave and reduce the N=O bond in NDMA, generating UDMH. Then the N—N bond in UDMH is cleaved to form DMA and ammonium.

1. Introduction

N-nitrosodimethylamine (NDMA) is reasonably anticipated to be a human carcinogen (National Toxicology Program, 2011). It was detected in many drinking water wells throughout California of USA and Canada, and also in treated drinking water and waste water (California Department of Public Health, 2011; Mitch et al., 2003). Subsequent studies have demonstrated that NDMA is one disinfection by-product of chlorination and chloramination of water and waste water (Choi and Valentine, 2002; Mitch and Sedlak, 2002). Besides, it can form during the ozonation and other treatments with strong oxidants (Andrzejewski et al., 2008; Von Gunten et al., 2010; Yang et al., 2009). It also aroused increasing concern among public health agencies. The U.S. Environmental Protection Agency (EPA) classified it into the group B2 as a "Probable human carcinogen" and estimated it had a 10^{-6} carcinogenic risk from 0.7 ng L^{-1} oral exposure (U.S.EPA, 1993). So it is necessary to develop some effective methods to remove it from drinking water.

Reductive processes with or without the augment of hydrogen have been investigated as alternative treatment methods for NDMA removal. Catalysts, including Pd, Pd—Cu,

Pd—In, Ni and NiB, have shown the abilities to reduce NDMA with hydrogen (Davie et al., 2006, 2008; Frierdich et al., 2008; Frierdich et al., 2009). NDMA is reduced by the Pd-based catalysts with half lives of several hours under hydrogen. NDMA and dihydrogen are adsorbed and activated on the Pd surface. The active hydrogen atom cleaves the N—N bond, resulting dimethylamine (DMA) and ammonium (NH_4^+) as the products (Davie et al., 2006, 2008). Additions of Cu or In to Pd facilitate the NDMA activation, increasing the observed reaction rate (Davie et al., 2006, 2008). With hydrogen, NDMA is reduced in several minutes by the Ni-based catalysts. The dihydrogen and NDMA N—N bond break at the Ni surface, generating the adsorbed atom hydrogen, surface-bond dimethylamide and nitric oxide fragments. The three will further react to generate the observed DMA and inorganic nitrogen species (NH_4^+ or N_2) (Frierdich et al., 2008, 2009). Hydrogen supply becomes a barrier to the application of these catalytic hydrogenation technologies. As hydrogen is flammable, safety assurance measures have to be taken in each operational link.

Zero-valent iron (Fe(0)) and nickel enhanced iron both transform NDMA to DMA and NH_4^+ without hydrogen. The electron is transferred from iron to water, generating the monatomic hydrogen. The hydrogen atom is activated on the iron or nickel surface and reacts with NDMA (Odziemkowski et al., 2000). Pseudo-first-order kinetics was observed for iron. Addition of nickel greatly enhanced the transformation rate but the kinetics varied over time (Gui et al., 2000). However, the reaction rate of NDMA reduction by iron is quite slow with the average half- life of 13 ± 2 h. The deficiencies of iron cause the need of finding the other reductants. Zero-valent zinc (Zn(0)) is capable of degrading carbon tetrachloride (Boronina et al., 1995), chlorinated ethylene, chlorinated acetylene (Arnold and Roberts, 1998) and 1,2,3-Trichloropropane (Salter-Blanc and Tratnyek, 2011; Sarathy et al., 2010). With a much lower reduction potential than Fe(0) ($Eo_{Fe/Fe}^{2+} = -0.440$, $Eo_{Zn/Zn}^{2+} = -0.763$) (Yang, 1982), Zn(0) may have a better performance on the reduction of NDMA. To our knowledge, there is no systematic study on the reduction of NDMA with Zn(0) in water.

The objectives of this study were to determine the efficiency and kinetics of NDMA reduction with Zn(0), quantify the intermediate and final products during the reduction of NDMA with Zn(0) and propose the reaction mechanism of the reduction of NDMA with Zn(0).

2. Materials and methods

2.1. Chemicals and materials

Most experiments were conducted using deionized water (DI water). DI water and all solutions used in the anaerobic experiment were degassed before use with high purity N_2 for $1 h \cdot 200 mL^{-1}$ and stored in a vacuum glove box. NDMA used in degradation experiments was synthesized using the method described by Hu and Ma (Hu and Ma, 1980). Its purity was confirmed by GC—MS (Agilent 6890-5973N) (Figure S1). Dimethylamine hydrochloride (DMA·HCl, 99%) was purchased from Acros Organics. NDMA ($200 \mu g mL^{-1}$ in methanol) used as standard was purchased from Supelco. 1,1-dimethylhydrazine

(unsymmetrical dimethylhydrazine, UDMH, 98%) was purchased from Tokyo Chemical Industry. All chemicals were used without further purification.

The zinc powder used in the study was obtained from Basifu Chemical Co., Ltd (Tianjin, China). Its surface area, measured by the BET method, was $5.71 m^2 g^{-1}$. The material was used without prior cleaning. It contained 10% ZnO and 90% Zn as confirmed by Xray diffraction (XRD) analysis. The iron powder was purchased from TanJin Bodi Chemical Holding Company. Its surface area was $2.06 m^2 g^{-1}$ (measured by the BET method).

2.2. Experimental procedures

Each batch reaction was conducted in 100 mL stoppered conical flask. In the efficiency and pH effect experiments, the zinc powders were added in the flasks filled with 100 mL NDMA solution of the concentration of $100 \mu g L^{-1}$, and then the glass caps were tightly plugged. The flasks were placed on a rotary shaker (SHA-EA, Jintan jingda apparatus factory, China) and covered with a lid to keep in the dark during the reaction. Samples were withdrawn from the reactor at a certain time and filtered through 0.22 μm membrane using a vacuum pump to separate unreacted zinc to terminate the reaction. The initial solution pH was adjusted by adding sodium hydroxide or hydrochloric acid to the NDMA solution, the solution pH during the reaction was measured after the termination of the experiment.

The procedure of the experiment without NDMA was similar by adding DI water to flasks instead of NDMA solution, and only the pH and zinc ion were detected. In the product studies, the initial NDMA concentration was increased to $0.05 mmol L^{-1}$ in order to determine the intermediate and ultimate products better.

In the anaerobic experiment, all preparations were conducted in a vacuum glove box. NDMA solutions were added to the flasks containing zinc powders, each flask was completely sealed and took out of the glove box. The flasks were put into the rotary shaker to react. The following procedure and detection were the same as the experiments with oxygen.

2.3. Analysis

NDMA was analyzed using a Shimadzu LC-10A high-performance liquid chromatography with an ultraviolet detector. The detection followed the method developed by Chen et al (Chen et al., 2007). The practical detection limit with this method was $0.1 \mu g L^{-1}$. As for UDMH measurement, the liquid samples were pretreated by 4-nitrobenzaldehyde (Denisov et al., 2004). The derived water samples were separated by the C18 column and detected by the ultraviolet detector. The wavelength was chosen as 390 nm. The acetonitrile and water with a volume ratio of 4:1 were taken as the mobile phases, the detection limit was $0.5 \mu g L^{-1}$.

DMA concentration was measured by an Agilent GC7890/FID after derivatization with benzenesulfonyl chloride using the improved method (Yang et al., 2010), which was based on the one developed by Sacher et al. (1997). The detection limit of DMA using this method was $0.5 \mu g L^{-1}$. The dissolved zinc ion was determined by inductively coupled plasma atomic emission spectrometer (ICP-AES, Optima5300DV, Perkin