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Hydrogen production from the dissolution of nano zero valent iron and its effect on anaerobic digestion

Yu-Xi Huang [a], Jialiang Guo [a], Chunyang Zhang [b], Zhiqiang Hu [a, *]

[a] Department of Civil and Environmental Engineering, University of Missouri, Columbia, MO 65211, USA
[b] School of Life Science, Shandong University of Technology, Shandong Province, China

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ABSTRACT

Nano zero valent iron (NZVI) has shown inhibition on methanogenesis in anaerobic digestion due to its reductive decomposition of cell membrane. The inhibition was accompanied by the accumulation of hydrogen gas due to rapid NZVI dissolution. It is not clear whether and how rapid hydrogen release from NZVI dissolution directly affects anaerobic digestion. In this study, the hydrogen release kinetics from NZVI (average size = 55 ± 11 nm) dissolution in deionized water under anaerobic conditions was first evaluated. The first-order NZVI dissolution rate constant was 2.62 ± 0.26 h^{-1} with its half-life of 0.26 ± 0.03 h. Two sets of anaerobic digestion experiments (i.e., in the presence of glucose or without any substrate but at different anaerobic sludge concentrations) were performed to study the impact of H_2 release from rapid NZVI dissolution, in which H_2 was generated in a separate water bottle containing NZVI (i.e., ex situ H_2 or externally supplied from NZVI dissolution) before hydrogen gas was introduced to anaerobic digestion. The results showed that the H_2 partial pressure in the headspace of the digestion bottle reached as high as 0.27 atm due to rapid NZVI dissolution, resulting in temporary inhibition of methane production. Nevertheless, the 5-d cumulative methane volume in the group with ex situ H_2 production due to NZVI dissolution was actually higher than that of control, suggesting NZVI inhibition on methanogenesis is solely due to the reductive decomposition of cell membrane after direct contact with NZVI.

1. Introduction

Nano zero valent iron (NZVI) has antimicrobial activities against a broad range of microorganisms by disrupting cell membrane and metabolic functions. Iron is a strong reductant ($E^{\circ}_{Fe^{2+}/Fe^0} = -0.447$ V vs. standard hydrogen electrode). The mode of action of NZVI is through reductive decomposition of cell membrane due to strong reducing conditions at the NZVI surface (Kim et al., 2011; Lee et al., 2008). NZVI is therefore effective in killing both Gram-positive and Gram-negative bacteria (Diao and Yao, 2009). As oxidation–reduction potential (ORP) decreases with increased NZVI concentration (Shi et al., 2011), the direct interactions between the reactive surfaces of NZVI and bacterial cells are primarily responsible for the disruption of cell membrane. Not surprisingly, although it is increasingly used in environmental remediation (Bai et al., 2009; Kanel et al., 2006; Machado et al., 2013), industrial wastewater treatment (Li et al., 2014) and odor control in biosolids treatment (Li et al., 2007), direct use of NZVI in anaerobic sludge digestion may result in complete methanogenesis inhibition (Yang et al., 2013).

Anaerobic digestion includes mainly four stages (Gujer and Zehnder, 1983; Kaspar and Wuhrmann, 1978; Mosey, 1983). The first stage is hydrolysis in which macromolecules such as proteins, carbohydrates and lipids are decomposed to long chain fatty acids, amino acids and simple sugars. These products are degraded further into volatile fatty acids (VFAs), such as propionic acid and butyric acid during acidogenesis. Small amount of hydrogen (H_2) will also be produced in this process. In the third stage called acetogenesis, acetate is generated from carbon dioxide and an electron source from organic or inorganic sources such as hydrogen. The final stage of anaerobic digestion is methanogenesis, in which methane is produced through acetoclastic ($CH_3COOH \rightarrow CH_4 + CO_2$) and hydrogenotrophic methanogenesis ($4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$). In anaerobic digestion, H_2 partial pressure (pH_2) has to be kept at a very low level so that the process

* Corresponding author. E2509 Lafferre Hall, University of Missouri, Columbia, MO 65211, USA.
E-mail address: huzh@missouri.edu (Z. Hu).

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of acidogenesis is thermodynamically feasible. This is normally achieved by hydrogenotrophic methanogenesis where methane serves as the sink for H_2. Alternatively, there is another potential H_2 sink through homoacetogenesis in which H_2 and carbon dioxide (CO_2) are used to produce acetate ($4H_2 + 2CO_2 \rightarrow CH_3COOH + 2H_2O$). Although homoacetogenesis usually cannot compete with hydrogenotrophic methanogenesis, studies have shown that at high pH_2, homoacetogenesis is favored (Demirel and Scherer, 2008). In addition, the growth rate of homoacetogens on H_2 and CO_2 is higher than that of acetogens growing on organic substrates as electron acceptors, which gives homoacetogens advantages over other acetogens under high pH_2 conditions (Saady, 2013).

While recent studies showed that NZVI disrupted cell membranes and inhibited methanogenesis, the results also suggested that the rapid H_2 production due to NZVI dissolution might contribute to methanogenesis inhibition and lead to bacterially controlled hydrogenotrophic processes (Lee et al., 2008; Marsalek et al., 2012; Yang et al., 2013). However, these two effects are difficult to distinguish when NZVI is directly applied to anaerobic digestion systems.

In anaerobic digestion, the anaerobic reduction pathways in the presence of hydrogen due to NZVI dissolution depend on the available terminal electron acceptors and hydrogen gas concentration, as homoacetogenesis has a higher H_2 concentration threshold (400 nM) than methanogenesis 10.9 (± 3.3) nM, respiratory dechlorination 2.2 (± 0.9) nM, and sulfate reduction (1–1.5 nM) (Yang and McCarty, 1998). Organisms such as sulfate reducing bacteria (SRB) using acceptors associated with greater energy production have lower hydrogen concentration thresholds than organisms using electron acceptors that yield less energy from hydrogen oxidation. Since biological methane production is one of the major goals in anaerobic digestion, questions therefore remain as to whether and how hydrogen production from NZVI dissolution will directly affect methanogenesis and other important biochemical processes in anaerobic digestion. NZVI with higher specific surface area is highly reactive and releases H_2 within a short time, which could create a significant H_2 shock to anaerobic digestion. Meanwhile, characteristics such as particle size, crystallinity and surface oxidation degree largely determine the reactivity of NZVI. For instance, complete oxidation of Fe(0) in highly disordered NZVI to generate H_2 lasted for less than two weeks, while oxidation of crystalline NZVI could last for one year (Liu et al., 2005a, 2005b). A half-life time of 90–180 days has been reported for commercial NZVI (~100 nm) at pH 10.6 (Liu and Lowry, 2006). Still, little work has been done on the measurements and modeling of kinetics of NZVI dissolution and hydrogen evolution from water.

The main objective of this research was to determine whether the rapid hydrogen production from NZVI dissolution causes any methanogenesis inhibition. To this end, we used freshly prepared NZVI to measure the rate of NZVI dissolution in deionized (DI) water through H_2 gas monitoring. Thereafter, we applied a dissolution model and determined the first-order dissolution rate constant of NZVI. By applying ex situ hydrogen production from NZVI dissolution, we finally determined the direct impact of hydrogen production from NZVI dissolution on anaerobic digestion.

2. Materials and methods

2.1. NZVI synthesis and characterization

NZVI stock suspensions were prepared freshly through a method reported in the literature (He et al., 2006). Briefly, a 0.2% (w/w) sodium carboxymethyl cellulose (CMC, capping agent, Sigma–Aldrich, St. Louis, MO) solution was made by dissolving CMC in DI water. Then 200 mL of the CMC solution was purged with nitrogen gas for 20 min before the addition of 50 mL of 0.625 M ferrous chloride solution under nitrogen gas purging. Thereafter, 31.25 mL of 4 M sodium borohydride ($NaBH_4$, Sigma) was added drop wise to the above solution at room temperature with vigorous stirring. The final concentrations of NZVI and CMC in the stock solution were 0.11 M and 0.14% (w/w), respectively. To avoid oxidation, the NZVI stock solution was purged with nitrogen gas throughout the synthesis process following the protocols described elsewhere (Lee et al., 2008; Li et al., 2010). The prepared NZVI particles had an average size of 55 ± 11 nm, which were characterized by transmission electron microscopy and Image J software (from rsbweb.nih.gov) (Yang et al., 2013).

2.2. Kinetics of H_2 release from NZVI dissolution

To determine the kinetics of NZVI dissolution and H_2 production, a batch study was conducted in a series of 700 mL glass bottles by adding aliquots of NZVI stock suspension in DI water to the final concentrations of 1, 2, 10 and 15 mM, respectively. All treatments were conducted in a dark room in triplicate under mesophilic conditions (37 °C). To minimize the effect of headspace, there was only 20 mL headspace in each bottle. Soon after the addition of NZVI, the bottle was capped tightly. While the mixed liquor in the bottle was magnetically stirred at 300 rpm, hydrogen produced from NZVI dissolution was monitored real-time by an AER-200 respirometer (Challenge Technology, AK), which has a resolution of 0.05 mL and maximum rate of 500 mL h^{-1}.

2.3. Modeling of NZVI dissolution and hydrogen production and determination of dissolution rate constant

In a system that is stirred by turbulence, the flux of NZVI dissolution and subsequent hydrogen release is controlled by the rate of transport across the laminar sub-layer on the NZVI solid boundary (Supporting information, Fig. S1). In other words, because molecular diffusion across the sub-layer is slower than turbulent diffusion by several orders of magnitude, transport across the laminar sub-layer is the limiting step and the rate at which mass is supplied from the boundary to the fluid is set by the rate at which mass diffuses across the laminar sub-layer. The concentration directly at the boundary, $C_{(z\,=\,0)} = C_{eq}$, is set by chemical equilibrium. Due to vigorous mixing, it is assumed that the hydrogen concentration in water (C) is uniform if $z > \delta_s$. Conservation of mass for the bulk fluid in a system with a volume of V is then

$$V\frac{\partial C}{\partial t} = -D_m A\frac{C - C_{eq}}{\delta_S} \quad (1)$$

Where D_m is diffusion coefficient and A is cross-sectional area of the laminar sub-layer. By rearranging,

$$\frac{\partial C}{\partial t} = -\frac{D_m A}{V\delta_S}(C - C_{eq}) = -k(C - C_{eq}) \quad (2)$$

Where k is the dissolution rate constant. With initial condition, $C_{(t\,=\,0)} = 0$,

$$C = C_{eq}\left(1 - e^{-kt}\right) \quad (3)$$

Furthermore, the gaseous hydrogen concentration is related to the dissolved hydrogen concentration by Henry's law. Due to fast hydrogen production from NZVI dissolution and very low hydrogen