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Iron sulfide attenuates the methanogenic toxicity of elemental copper and zinc oxide nanoparticles and their soluble metal ion analogs

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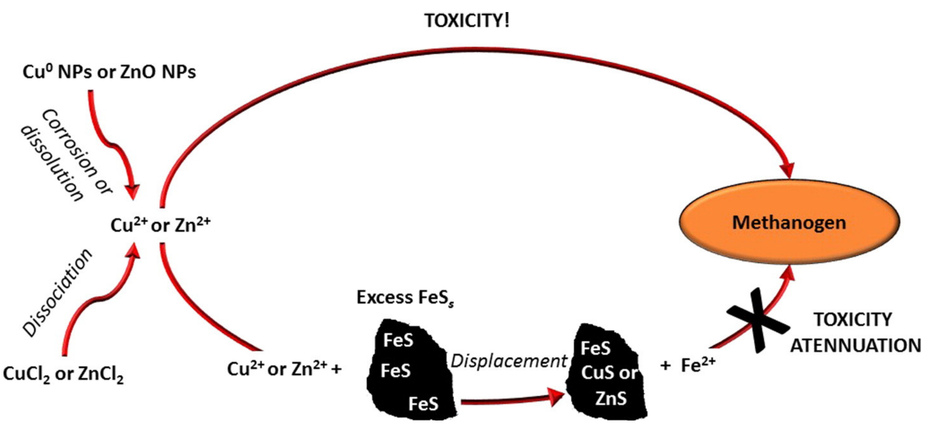
HIGHLIGHTS

- FeS effectively attenuates Cu^0 NP and ZnO NP toxicity.
- FeS effectively attenuates CuCl$_2$ and ZnCl$_2$ toxicity.
- Finer fraction of FeS increases toxicity attenuation effect.
- FeS attenuation effect is limited by its solubility.

GRAPHICAL ABSTRACT



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ABSTRACT

Elemental copper (Cu^0) and zinc oxide (ZnO) nanoparticle (NP) toxicity to methanogens has been attributed to the release of soluble metal ions. Iron sulfide (FeS) partially controls the soluble concentration of heavy metals and their toxicity in aquatic environments. Heavy metals displace the Fe from FeS forming poorly soluble metal sulfides in the FeS matrix. Therefore, FeS may be expected to attenuate the NP toxicity. This work assessed FeS as an attenuator of the methanogenic toxicity of Cu^0 and ZnO NPs and their soluble salt analogs. The toxicity attenuation capacity of fine (25–75 μm) and coarse (500 to 1200 μm) preparations of FeS (FeS-f and FeS-c respectively) was tested in the presence of highly inhibitory concentrations of CuCl$_2$, ZnCl$_2$ Cu^0 and ZnO NPs. FeS-f attenuated methanogenic toxicity better than FeS-c. The results revealed that 2.5× less FeS-f than FeS-c was required to recover the methanogenic activity to 50% (activity normalized to uninhibited controls). The results also indicated that a molar FeS-f/Cu^0 NP, FeS-f/ZnO NP, FeS-f/ZnCl$_2$, and FeS-f/CuCl$_2$ ratio of 2.14, 2.14, 4.28, and 8.56 respectively, was necessary to recover the methanogenic activity to >75%. Displacement experiments demonstrated that CuCl$_2$ and ZnCl$_2$ partially displaced Fe from FeS. As a whole, the results indicate that not all the sulfide in FeS was readily available to react with the soluble Cu and Zn ions which may explain the need for a large stoichiometric excess of FeS to highly attenuate Cu and Zn toxicity. Overall, this study provides evidence that FeS attenuates the toxicity caused by Cu^0 and ZnO NPs and their soluble ion analogs to methanogens.

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1. Introduction

Engineered nanoparticles (NPs) are man-made materials with at least one dimension <100 nm. Copper-based (Cu-based) and zinc oxide (ZnO) NPs are applied in several industrial processes or commercial products. Cu-based NPs are used in products such as wood preservatives, catalysts, printable electronics, or antimicrobials (Wang et al., 2013); likewise, Cu-based NPs are the byproduct of the chemical and mechanical polishing in the semiconductor industry (Golden et al., 2000). ZnO NPs are also applied in industrial processes and extensively used in consumer products such as sunscreens, cosmetics, and bottle coatings due to their ultraviolet blocking properties and visible transparency (Klaine et al., 2008).

The majority of NPs applied in consumer products are likely to be disposed into the sewer (Kim, 2014). Therefore, NPs will end up in biological processes such as aerobic activated sludge of wastewater treatment plants. Studies investigating the fate of NPs in wastewater treatment have found accumulation of NPs in activated sludge solids (Westerhoff et al., 2013). The accumulation of NPs may have toxic effects not only on the activated sludge microorganisms, but also on the microbial cultures involved in the stabilization of the waste sludge by anaerobic digestion, such as methanogens.

Recent research has consistently shown that elemental copper (Cu^0) and ZnO NPs are toxic to methanogens (Gonzalez-Estrella et al., 2015; Gonzalez-Estrella et al., 2013; Mu et al., 2012; Otero-González et al., 2014a). Results have also indicated that the soluble ions released by NPs cause toxicity (Luna-delRisco et al., 2011; Mu et al., 2011). Recently it was shown that biogenic sulfide (S^{2-}) produced by sulfate reduction decreased the toxic effect of Cu^0 and ZnO NPs (Gonzalez-Estrella et al., 2015). Soluble ions released from these types of NPs are hypothesized to precipitate with the sulfide. These findings establish that biogenic S^{2-} from sulfate reduction reliably attenuate Cu^0 and ZnO NP toxicity to methanogens. Other potential sources of S^{2-} present in anaerobic environments may also play a similar attenuating role.

Iron sulfides are one of the most common forms of sulfide on the Earth's crust (Muyzer and Stams, 2008). Iron sulfides, along with manganese sulfide, is one of the largest reservoirs of sulfides in aquatic sediments (Di Toro et al., 1992). The oxidization of organic matter in anaerobic environments provides the conditions for the bio-reduction of sulfate and Fe (III) yielding $S^{2-}$and Fe^{2+} (Morse et al., 1987), which react with each other to form iron sulfide (FeS) and pyrite (FeS_2) (Haaijer et al., 2012; Morse et al., 1987). FeS is a poorly soluble mineral ($\log K_{s0} = -16.84$ (Benjamin, 2002)) that commonly interacts other heavy metals in aquatic sediments (Besser et al., 1996); therefore, it regulates the concentration of heavy metals in these environments (Casas and Crecelius, 1994).

When divalent metals with more affinity for S^{2-} such as cadmium, copper, lead, mercury, or zinc are present in anaerobic sediments, the Fe^{2+} of FeS can be displaced by these divalent metals forming more stable metal sulfides and releasing Fe^{2+} cations to the aqueous phase (Peng et al., 2009). For instance, Cu^{2+} and Zn^{2+} have higher stability constants for sulfide (CuS ($\log K_{s0} = -35.96$) and ZnS ($\log K_{s0} = -21.97$) (Benjamin, 2002)) than FeS; thus, Cu^{2+} and Zn^{2+} will displace the Fe of FeS to form CuS and ZnS. This mechanism is illustrated in Eq. (1)

$$FeS + Me^{2+} \rightarrow MeS + Fe^{2+} \quad (1)$$

where Me^{2+} are heavy metals such as Cu^{2+} or Zn^{2+}. Simpson et al. (2000) experimentally demonstrated the immobilization of Cd, Cu, and Zn by reaction with FeS.

Reactions of FeS with heavy metals have a key role controlling the toxicity in aquatic sediments (Allen et al., 1993; Casas and Crecelius, 1994; Di Toro et al., 1992; Di Toro et al., 1990). Consequently, a similar approach could be taken to attenuate the methanogenic toxicity of Cu^0 and ZnO NPs and their soluble metal Ion analogs by adding FeS to anaerobic reactors with presence of these inhibitors. If the toxic Cu^{2+} and Zn^{2+} ions released by Cu^0 and ZnO nanoparticles displace the Fe^{2+} in FeS to form stable metal sulfides, Cu^0 and ZnO toxicity can be expected to be attenuated by FeS. The purpose of this work was to evaluate the attenuation of Cu^0 and ZnO NP toxicity to methanogens by FeS.

2. Material and methods

2.1. Chemicals

All NPs were acquired as powders. Cu^0 NPs (40–60 nm, 99%) were purchased from Sky-Spring Nanomaterials Inc. (Houston, TX), ZnO NPs (100 nm, 99%), $CuCl_2 \cdot H_2O$ (99%), $ZnCl_2$ (98%), sodium acetate (99.9%), and $Na_2S \cdot 9H_2O$ (>98%) were acquired from Sigma Aldrich (St. Louis, MO, USA). $FeCl_2 \cdot 4H_2O$ (>99%) was acquired from Fisher-Scientific. CH_4 standard gas (99%) was acquired from Air Liquid America (Plumstedsville, PA, USA).

2.2. Nanoparticle dispersions and metal solutions

ZnO and Cu^0 NP stock dispersions were sonicated (DEX® 130, 130 W, 20 kHz, Newtown, CT) at 70% amplitude for 5 min. No dispersant agent was supplied to the stock solutions. ZnO and Cu^0 NP stability in anaerobic media has been previously described (Gonzalez-Estrella et al., 2013; Otero-González et al., 2014a). The studies report a PSD of 685 ± 64 and 958 ± 34 for ZnO and Cu^0 NP, respectively, and a z-potential of −26.3 ± 0.8 and −14 .9 ± 0.9 for ZnO and Cu^0 NP, respectively. Previous transmission electron microscopy (TEM) analysis reported an average particle size of 48.5 ± 27.8 nm for ZnO NPs (Otero-González et al., 2014a). TEM analysis applying the same methodology showed an average particle size of 50 ± 15.0 nm for Cu^0 NP (Fig. S1, Supporting Information). Stock $CuCl_2$ and $ZnCl_2$ solutions were prepared by dissolving the salts in 0.01 M HCl.

2.3. FeS synthesis and characterization

FeS was synthesized by adapting a methodology previously used (Patterson et al., 1997). FeS was prepared by mixing an equimolar concentration of sodium sulfide and iron chloride ($FeCl_2$) for 10 min. Next, the suspension was centrifuged in 50 mL vials at 4000 rpm for 20 min. The supernatant was discarded and the pellet of FeS was resuspended with 50 mL ethanol. Subsequently, the suspension was subjected twice to a centrifuging (4000 rpm for 20 min) and rinsing procedure to eliminate the majority of the water. Next, the supernatant was discarded and the pellet was rapidly transferred to test tubes. The test tubes were sealed and flushed with N_2 gas until the pellet was completely dry. After drying the pellet, the product was composed of a coarse preparation of FeS particles (FeS-c). Half of the FeS-c was agitated in the test tube vigorously with a vortex mixer until the particle size was decreased to a fine preparation of FeS particles (FeS-f). The synthetized FeS preparations were kept in sealed flask with N_2 atmosphere to prevent oxidation. The particle size of FeS-c and FeS-f particles was evaluated by SEM analyses. The images of the SEM analyses of FeS-c and FeS-f are shown in Fig. 1. The analyses indicated that FeS-c had a particle size range of 500 to 1200 μm, whereas the range FeS-f particles were 25–75 μm. It should be noted that a few coarse pieces of FeS can be observed in FeS-f as shown in Fig. 1B. Fe content of FeS was determined by measuring the soluble Fe after a microwave digestion assisted treatment. The samples reveled a content of 0.45 mg Fe mg solid^{-1}. Therefore, assuming that the concentration of Fe and S in the solid was stoichiometric, the purity of the synthesized FeS is 71.3%. A sample of each fraction was characterized by X-ray diffraction (XRD) analyses. XRD analysis revealed an amorphous composition by the lack of any clear X-ray diffraction signals in the samples (Fig. S2). An additional energy-dispersive X-ray spectroscopy (EDS) analysis, revealed that the surface of the material contained 12.5 ± 2.07% (atomic weight) of S