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In-situ prevention of hydrogen sulfide formation during anaerobic digestion using zinc oxide nanowires

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ABSTRACT

The utilization of Anaerobic Digestion (AD) technology for biogas and energy generation is often hindered by high concentration of sulfur-containing compounds in wastewater and consequential hydrogen sulfide (H_2S) in biogas. In this work, we demonstrated a process, where independent mechanisms of anaerobic microorganisms and an inorganic reactive adsorbent (zinc oxide nanowires) worked synergistically to remove soluble sulfide (HS^-) and prevent H_2S formation during AD. Using a model aqueous sodium sulfide (Na_2S) system, the nanowires (dosage 1 g/L) effectively removed sulfides from the Na_2S solution to a maximum of 625 mg S^{2-}/L per gram of ZnO. During 24 h and 3-day long (involving three consecutive sulfate feeding cycles) AD studies using anaerobic microbial medium (2 g/L SO_4^{2-} and 1 g/L ZnO), no decrease in methanogenic activity and biogas production were observed using the ZnO nanowires, indicating that the nanowires can reduce the sulfide toxicity during AD. The post-process analysis of the recovered nanomaterial using energy-dispersive X-ray spectroscopy and X-ray diffraction showed the presence of sulfur and zinc sulfide (ZnS), respectively, validating HS^- removal by the nanowires. This process intensification approach of combining AD and H_2S removal into a single process step will help extend AD technology to high sulfate containing wastewaters.

1. Introduction

Anaerobic digestion (AD) technology is widely used to treat municipal waste, as well as industrial and food processing wastewaters prior to discharge. Biogas, a major product of AD, is the most sustainable of biofuels and is in a starting phase of an exponential market growth curve. It can be used to produce electricity, heat, and transport fuel [1]. Also, the semi-solid byproduct of this process (digestate) has a high content of nutrients, which can be used in agriculture directly as a fertilizer or processed into compost to increase its quality [2,3]. Thus, anaerobic digesters offer many potential benefits to both the industry and the environment. Therefore, the demand on the AD technology to be robust across a wide range of incoming waste streams and the need for biogas of consistent quality to feed gas generator sets for electricity production are increasing.

The biggest obstacle for successful application of AD for energy generation is the presence of hydrogen sulfide (H_2S) in biogas. Elevated levels of H_2S in biogas are not only corrosive to the piping, turbines, and other equipment associated with the biogas industry [4], but also can lead to harmful sulfur dioxide emissions during combustion of the biogas. Concentrations of H_2S in raw biogas are typically between 50 mg/L and 5000 mg/L. Removing H_2S from biogas [5] or, more preferably, minimizing the formation of H_2S in biogas [6–8] is required to protect downstream equipment such as turbines and fuel cells. In terms of equipment tolerances, H_2S concentrations must be between 200–500 mg/L for combustion of biogas in an internal combustion engine (co-generation). Direct injection of biogas into the natural gas pipeline network as “upgraded bio-methane” (natural gas equivalent) would require H_2S reduction down to below 4 mg/L.

Hydrogen sulfide in biogas is produced by sulfate-reducing bacteria, commonly present in the anaerobic sludge. Sulfate reducing bacteria grow in the presence of sulfate, sulfite, or thiosulfate in the incoming waste stream, producing soluble sulfide (Table S1 in Supplementary materials). The soluble sulfide, under proper conditions, is liberated as H_2S gas (Eq. (1)). One possible option to reduce the H_2S formation is to remove soluble sulfide (HS^-) as it is being formed.

$$HS^-_{aq} + H^+_{aq} \rightarrow H_2S_g \quad (1)$$

Some waste streams contain high concentration of sulfates, which will lead to elevated levels of H_2S in biogas as well as a reduction in the efficiency or an irreversible inhibition of the anaerobic digestion [7–12]. In order for such waste streams to be treatable, it is crucial to develop techniques that minimize the formation of soluble sulfide in situ.

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Table 1
Methods of in situ reduction of sulfides during AD.

#	Method	Reference
1	pH elevation to reduce formation of toxic undissociated H_2S	[10]
2	Precipitation of sulfides using iron salts	[11]
3	Oxidation of sulfides using chemical oxidation agents	[11,12]
4	Chemical inhibition of sulfate-reducing bacteria	[13]
5	Biological sulfide removal using sulfide-oxidizing bacteria (micro-aeration)	[14]
6	Biological sulfide removal using sulfide-oxidizing photosynthetic bacteria	[15]
7	Biological denitrifying sulfur removal	[16]

2. H_2S removal strategies

There are two general H_2S removal strategies from biogas: 1) post-treatment of biogas after anaerobic digestion and 2) in-situ removal during anaerobic digestion. The most common commercial methods for hydrogen sulfide removal from the biogas are: biological filters, iron oxide pellets, impregnated activated carbon, and scrubbing using water, sodium hydroxide, etc. Scrubbing and recirculating digester biogas is a common practice to reduce the content of H_2S in biogas [5]. However, this is an expensive option requiring additional process equipment at a significant cost. Various methods have been used for in situ reduction of sulfides during the digestion process, as listed in Table 1.

Chemical methods (Table 1, methods 1–4), although efficient in mitigating the negative effect of sulfides, require constant introduction of chemicals, as well as additional equipment and process steps. Thus, these methods are unsustainable and add significantly to the cost of the AD treatment [17]. Recently, several biological methods of sulfide removal have emerged as a promising alternative (Table 1, methods 5–7; detailed discussion of the methods is available in Supplementary materials). However, these methods are in their early stages of development and require a significant research effort to become a robust technology. Thus, there is still a great need for a cost-efficient, sustainable, and robust technology for sulfide removal during AD.

In this work, a hybrid process was developed for in-situ H_2S removal during AD by adding a nanostructured reactive adsorbent consisting of zinc oxide nanowires (ZnO NWs). ZnO has been used as an efficient and regenerable adsorbent in the high temperature desulfurization of coal-derived fuel gas [18] and syngas [19]. ZnO is favorable among the other metal oxides (e.g., iron oxide) due to its high equilibrium constant for the ZnO-H_2S reaction as well as its high reactivity and the ability of the resulting ZnS to be regenerated. The advantages of using ZnO NWs instead of ZnO powders are due to their monocrystalline nature and faceting, which improves the reactivity of the material. They are also resistant to sintering and capable of maintaining a high surface area. The reactive adsorbent in the form of pellets is placed in a water-permeable pouch (mesh 200, nylon) for easy recovery and introduced into the AD medium during the anaerobic digestion process. While the sulfate reducing bacteria are converting the sulfates in wastewater to HS^-, the nanowires are adsorbing the generated HS^-, preventing the formation of hydrogen sulfide gas. According to the following equations, the adsorbed HS^- reacts with ZnO to form ZnS, and water is formed as a byproduct.

$$HS^- + ZnO \rightarrow ZnS + OH^- \quad (2)$$

$$OH^- + H^+ \rightarrow H_2O \quad (3)$$

Our approach is expected to minimize the formation of H_2S in biogas by adsorbing HS^- in the waste water under ambient conditions, increase the biogas yield, reduce toxicity to the biomass, and make the AD operation more stable over a wide range of sulfate levels. This process can be a retrofit to the existing AD systems and does not add significantly to the operating cost.

Previous studies by Petzold et al. [20] describe the efficiency of a nanostructured catalyst in the hydrodesulphurization of diesel. In their work, it was shown that at elevated temperature, Ni nanoparticles decorating ZnO nanowires catalyze the cleaving of cyclic sulfur compounds and sequester the released sulfur in the form of NiS. The ZnO nanowires, in the presence of hydrogen, react with sulfur atoms from NiS sites forming ZnS and regenerating the nickel catalyst. While this previous work focused on the removal of sulfur compounds from cyclic structures in diesel at elevated temperature, the mechanism of sulfur removal using nanostructured reactive adsorbent can be potentially extended to remove HS^- ions under ambient conditions of anaerobic digestions processes.

The primary goal of this study is to evaluate the suitability and performance of ZnO NWs as an in situ reactive adsorbent of soluble sulfides formed during the AD process. In the first part of the study, the ability of the ZnO NWs to adsorb sulfides was tested in a model system consisting of aqueous solution of sodium sulfide (Na_2S). Sodium sulfide is primarily used in the pulp and paper industry in the Kraft process. In water at neutral pH, Na_2S hydrolyzes to yield hydroxide and hydrosulfide ions (Eq. (4)).

$$Na_2S + H_2O \rightleftarrows 2Na^+ OH^- + HS^- \quad (4)$$

Our approach is to use Na_2S in water as a controlled source of HS^- and monitor the level of sulfide in water in the presence of the nanostructured adsorbent. This test will be a validation for the adsorbent's capability to remove sulfides. Following this validation, we propose to test the adsorbent in situ during the AD process at varying sulfate levels in the wastewater.

3. Materials and methods

3.1. Materials

Calcium chloride, magnesium chloride, ammonium chloride, potassium phosphate monobasic, sodium sulfate were used as minerals and nutrients for anaerobic digestion tests and were purchased from Sigma-Aldrich. Sodium bicarbonate (Sigma-Aldrich) was used to adjust alkalinity. A proprietary inorganic salt mix (Respirometer Systems & Applications LLC, Springdale, AR, USA) was used as a source of trace elements. Sodium sulfide nanohydrate was purchased from Sigma-Aldrich and was used as a controlled source of HS^- ions. Sodium hydroxide and hydrochloric acid were purchased from Sigma-Aldrich and were used for pH adjustment. Ethanol was purchased from Sigma-Aldrich and was used as a model source of soluble COD.

Granular anaerobic sludge was kindly provided by Anheuser-Busch (St. Louis, MO). The sludge was a source for natural mixed anaerobic microbial community from an operating full-scale anaerobic digester treating brewery wastewater. The concentration of the bacteria in the sludge was measured as Volatile Suspended Solids (VSS) content and was determined to be 52.0 g/L. ZnO nanowires and ZnO nanowires with NiO particles were obtained from Advanced Energy Materials LLC − AdEM (Louisville, KY). AdEM produces the adsorbent using methods discussed in [20].

3.2. Analytical methods

Sulfide content in test solutions was determined colorimetrically using a commercial hydrogen sulfide test kit, Model HS-WR (Hach Company, Germany). Chemical analysis of sulfates was performed spectrophotometrically using commercial test kits and DR 3900 Spectrophotometer (Hach Company, Germany). Gas analysis was performed on SRI 8610C Gas Chromatograph (SRI Instruments Inc., Las Vegas NV) using HayeSep D column (Restek Corporation) and thermal conductivity detector (TCD) for methane and carbon dioxide detection; MXT-1 column (Restek Corporation) and flame photometric detector