Chemical Engineering Journal 297 (2016) 180–192

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Electrochemical sulfide removal by low-cost electrode materials in anaerobic digestion

Hongjian Lin, Nicholas Williams, Amelia King, Bo Hu *

Department of Bioproducts and Biosystems Engineering, University of Minnesota, 1390 Eckles Ave., St. Paul, MN 55108, USA

HIGHLIGHTS

- Carbon cloth and stainless steel AISI 304 were evaluated for sulfide oxidation.
- Both electrode materials showed complete sulfide removal of 10 mM at 3 V in 2 days.
- Carbon cloth had a stronger catalytic effect for sulfide oxidation in synthetic media.
- Ferrous and ferric marginally affected methane production, but mitigated sulfide.
- Stainless steel electrodes removed most sulfide without interfering methane production.

ARTICLE INFO

Article history:
Received 13 January 2016
Received in revised form 14 March 2016
Accepted 19 March 2016
Available online 25 March 2016

Keywords:
Sulfide removal
Electrochemical oxidation
Carbon cloth
Stainless steel
Biogas cleaning

ABSTRACT

Hydrogen sulfide removal is usually a necessary but costly step following the anaerobic digestion (AD) in order to upgrade biogas quality. Mitigating sulfide levels of biogas and digestate simultaneously in AD process will decrease the capital cost by eliminating standalone biogas upgrading facility. However, current *in situ* remediation methods, for instance, dosing of magnesium/sodium hydroxide, oxygen gas, iron salts, and nitrite or nitrate, potentially cause interference to biogas production and may intensively consume energy and chemicals. Here, an electrochemical remediation method was studied to use low-price electrode materials of carbon cloth and stainless steel AISI 304. These electrode materials at 3 V showed a complete removal of sulfide in 2 days in synthetic media of 10 mM sulfide solution. Operating conditions for carbon cloth and stainless steel electrodes as well as major intermediates of electrochemical reactions in bench-scale digester fed with dairy manure were examined to study the performances in sulfide removal and biomethane production. Based on the results, it was concluded that carbon cloth at 2 and 3 V, and stainless steel anodes at both 1 and 2 V have a potential of significantly removing hydrogen sulfide from biogas under continuous operation given sufficient electrode surface area. Intermittent 3 V voltage application (15 minutes per day) of stainless steel can remove most biogas hydrogen sulfide. The electrochemical sulfide oxidation and removal showed no/little negative effect on biomethane production, and therefore can be a promising technology for the AD industry to develop a cost-effective approach to producing sulfide free biogas.

1. Introduction

Anaerobic digestion (AD) is a commercialized technology to degrade organic-rich wastes and to generate biogas which mainly consists of methane and carbon dioxide. Sulfate (SO_4^{2-}) is a common component for a wide range of substrates, resulted from protein hydrolysis and mineralization as well as pH adjustment using sulfuric acid during biological/chemical processing. Sulfide (S^{2-}) is generated from sulfate in AD by sulfate-reducing bacteria in anaerobic respiration [1], and from sulfur-containing amino acids (e.g., cysteine and methionine) and their intermediates by enzymatic degradation [2]. Hydrogen sulfide (H_2S) is free to diffuse through cell membrane, and therefore a high concentration of H_2S tends to denature proteins inside the cytoplasm of methanogens by cross-linking polypeptide chains; in consequence, accumulated levels of sulfide/hydrogen sulfide may impose inhibition to methanogenesis for biogas generation, which has been frequently reported in literature [3]. The volatilized hydrogen sulfide in biogas or in ambient air causes irritating "rotten egg" odor, corrodes

---

* Corresponding author. Tel.: +1 612 625 4215 (O); fax: +1 612 624 3005.
E-mail address: bhu@umn.edu (B. Hu).

http://dx.doi.org/10.1016/j.cej.2016.03.086
1385-8947/

facility members, and poses health and safety threats to exposed humans and animals. It is a major nuisance in many biological processes where sulfate-reduction occurs. During the storage and utilization of biogas in internal combustion engines (e.g., gas turbines), storage tanks, boilers, and fuel cells, biogas will need to be upgraded to remove hydrogen sulfide, in order to reduce the risk of equipment corrosion and toxicity to catalysts [4]. Therefore, controlling sulfide level in AD medium is beneficial to biogas production, maintenance of reactors and facilities, and biogas upgrade. With a well-controlled sulfide level, the inhibition potentially caused by sulfide/hydrogen sulfide can be remediated, the threats of facilities corrosion can be decreased, and the subsequent requirement on biogas purification in terms of hydrogen sulfide removal may not be necessary and thus it reduces the overall cost of biogas production and application.

Half reactions	E_o' V *vs.* SHE	E_o' V *vs.* Ag/AgCl	
$S(s) + 2e^- + 2H^+ \rightarrow H_2S$	−0.272	−0.479	Reaction 1
$S(s) + 2e^- + H^+ \rightarrow HS^-$	−0.271	−0.478	Reaction 2
$S(s) + 2e^- \rightarrow S^{2-}$	−0.476	−0.683	Reaction 3
$SO_4^{2-} + 8e^- + 9H^+ \rightarrow HS^- + 4H_2O$	−0.213	−0.420	Reaction 4
$SO_4^{2-} + 8e^- + 10H^+ \rightarrow H_2S + 4H_2O$	−0.214	−0.421	Reaction 5
$SO_4^{2-} + 6e^- + 8H^+ \rightarrow S(s) + 4H_2O$	−0.194	−0.401	Reaction 6
$H_2SO_3 + 4e^- + 4H^+ \rightarrow S(s) + 3H_2O$	+0.036	−0.171	Reaction 7
$S_2O_3^{2-} + 8e^- + 8H^+ \rightarrow 2S(s) + 3H_2O$	−0.213	−0.420	Reaction 8
$nS(s) + 2e^- \rightarrow S_n^{2-}$	−0.319 ($n = 5$)	−0.526 ($n = 5$)	Reaction 9
$S_n^{2-} + (2n{-}2)e^- + nH^+ \rightarrow nHS^-$	−0.255 ($n = 5$)	−0.462 ($n = 5$)	Reaction 10

Most previous research focus on cleaning technology for biogas, which is to remove H_2S from gas stream in a separate operation unit after AD [4]. For example, adsorption using iron oxide has long been used in industry. Biological processes, e.g., biofilters, biotrickling filters and bioscrubbers (fixed-film and suspended growth), are widely tested for biogas hydrogen sulfide removal [5,6], in which defined sulfur-oxidation microorganisms grow in liquid phase or on packing media, and oxidize and remove sulfide from the inlet biogas. Some methods were also proposed for *in situ* sulfide/hydrogen sulfide removal from liquid media like sewer systems and digestate. Those methods include gas stripping using air or oxygen aeration to partially oxidize sulfide to elemental sulfur [7,8], to dose nitrate and nitrite to couple sulfide oxidation for its removal. Iron salts dosing is another method that can scavenge sulfide to precipitate insoluble sulfide minerals [9,10]. Intensive chemical consumption and cost, high energy input, and frequent waste disposal limit the application of those *in situ* methods. It will further be a concern if those methods are implemented in anaerobic digesters which have to produce biogas without compromise.

Electrochemical (anode oxidation) methods are recently introduced as an alternative way for sulfide control in geothermal brines, sewage, and caustic solutions [11]. Sulfide species are electrochemically active, and the oxidation decreases sulfide species concentration by forming a wide spectrum of intermediates and final products, including disulfide (S_2^{2-}), polysulfide (S_n^{2-}), sulfite (SO_3^{2-}), thiosulfate ($S_2O_3^{2-}$), and sulfate (SO_4^{2-}) (Reactions 1–10, [12,13]). For example, given the gold electrode tested in cyclic voltammetry [14], the oxidation of sulfide first forms mono-layer of elemental sulfur at low potential (−0.4 V *vs.* standard hydrogen electrode, or SHE) and then proceeds with the formation of multi-layer at higher potential (0.05 V *vs.* SHE). Polysulfide of mixed lengths is generated in the oxidation of sulfide as well as reduction of elemental sulfur during the reduction scan. Sulfide in geothermal brines was oxidized to elemental sulfur on graphite disk anode with controlled anode potential of 450 mV *vs.* saturated Ag/AgCl reference electrode [15]. It was reported that at relatively low electrode potentials, the deposited elemental sulfur then passivated the electrode surface and gradually decreased the rate of the sulfide oxidation. In fuel cell mode using potassium ferricyanide as electron acceptor, graphite granule electrodes removed sulfide in aqueous solution at a rate of 280 g-S/m^3/day [16], while simultaneously producing electrical power with the maximum level of 166 W/m^3. Sulfur was the predominant oxidation product, so the performance declined after 3-month operation as a result of excessive sulfur deposition on graphite granule anode [16].

To overcome the anode passivation by elemental sulfur, another study utilized the water electrolysis product of oxygen gas in anaerobic digester [17], with the anode made from titanium mesh with Ir-mixed metals oxides (MMO) coating and the cathode from stainless steel mesh. When the applied voltage was 3.5 V (35 mA for 3.5 L reactor), hydrogen sulfide concentration in biogas was lowered from between 200 and 3000 ppm to less than the detection limit of the method, and importantly, the methane production was improved by 10–25%. The biogas contained an appreciable amount of hydrogen gas but almost all oxygen gas was biologically consumed. Their results also showed the possibility of sulfide oxidation in single-chamber reactor configuration, which is a simpler design and has smaller internal resistance compared with two-chamber configuration that has a separator or membrane between electrodes to avoid mixing of reactants and products. An issue in scale-up of this technology is that the cost of MMO electrode material is high because of the use of platinum-group noble metals like Ru, Ir and Pt oxides [18,19]. The electrode configuration and implementation for well-distributed oxygen generation will be hindered by their limited availability and high price.

Less expensive electrode materials shall be offered for sulfide removal, and graphitic carbon cloth (CC) and stainless steels (AISI 304, 316, and 430) were identified for the current study. The main reasons for selecting these materials are as follows: first, both materials are potentially electrochemically active for oxygen evolution reaction [20,21], which may also display sulfide oxidation performance and be manipulated for indirect sulfide oxidation; second, both materials are easy to manipulate and offer a flat-sheet surface structure, which may increase relative electrode surface area compared to graphite rods, discs and granules, and facilitate the potential recovery and cleaning of electrode surface with