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Research article

Valorizing waste iron powder in biogas production: Hydrogen sulfide control and process performances

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ABSTRACT

Biogas is composed of different gases including hydrogen sulfide (H_2S), which is a hazardous gas that damages pipes and generators in anaerobic digestion system. The objective of this study was to control H_2S by waste iron powder produced by laser cutting machine in a steel and iron industry. Waste iron powder was mixed with dairy manure at a concentration between 2.0 and 20.0 g/L in batch experiments, while the concentration was varied between 1.0 and 4.0 g/L in bench experiment. In batch experiment, a reduction of up to 93% of H_2S was observed at waste iron powder of 2.0 g/L (T1), while the reduction was of more than 99% at waste iron powder beyond 8.0 g/L (T4 ~ T6). The total sulfide concentration (S_T) increased together with waste iron powder concentration and was fitted with a quadratic equation with a maximum S_T of 208.0 mg/L at waste iron powder of 20.2 g/L. Waste iron powder did not have significant effect on methane yield in batch and bench experiments. However, hydrolysis rate constant was increased by almost 100%, while the lag-phase period was reduced to half in test digesters compared to that in control digester. In bench experiment, H_2S concentration was reduced by 89% at 2.0 g/L, while 50% at 1.0 g/L. Therefore, waste iron powder was effectively removed H_2S and did not affect negatively anaerobic digestion process.

1. Introduction

Steel production is among the pillars of economic development as it has an important role in building construction, automobiles, shipbuilding, and industrial machinery sectors. However, various wastes are generated during steel production and processing, such as slag, sludge, and waste iron powder, that may cause serious environmental pollution (Das et al., 2007; Zhou and Yang, 2016). In this regard, started in the fiscal year of 2013, Japan Iron and Steel Federation has set a voluntary initiative to fight against global warming through “Commitment to a Low Carbon Society-Phase I” with four main components: eco-process, eco-product, eco-solution, and the developments of innovative technologies (“The Japan Iron and Steel Federation,” 2015). Waste iron powder is sparks of iron, a powder-like material, generated during laser cutting of iron and steel. This waste is often incinerated after treatment. However, due to the particular characteristic of this waste, powder, and the component, supposedly dominated by iron, waste iron powder is supposed to be recyclable in anaerobic digestion, which is an alternative technology to handle this waste in environmentally friendly approach.

Iron is among the essential trace metals used by biomass population in anaerobic digestion. It is the most abundant metal in methanogenic cells, followed consecutively by zinc, nickel, cobalt, molybdenum, and copper (Chen et al., 2008). Iron improves, among other things, anaerobic digestion process (Feng et al., 2014) by converting propionate and butyrate to acetate (Meng et al., 2013;

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Lin et al., 1998), improving process stability at a concentration of 100 mg/L of Fe (Zhang and Jahng, 2012), and increasing methane production at a concentration between 1 and 4 g/L of Fe powder (Liu et al., 2015). Furthermore, iron does not only limit the competition between sulfate-reducing bacteria (SRB) and methanogens, but also binds with sulfide forming iron sulfide (FeS). The binding of iron with sulfide is, obviously, reducing the sulfide or iron ions inside reactors and, thus, minimizing the risks of sulfide or iron inhibition to anaerobic microorganisms (Chen et al., 2008; Gonzalez-Silva et al., 2009). The effects of scrap iron or iron powder usage, obtained from machinery workshop, in anaerobic digestion has been reported in literature. For example, Zhang et al. (2011) reported that waste iron reduced the sulfide inhibition on methanogens, while Zhang et al. (2014) and Liu et al. (2015) found that waste iron accelerated hydrolysis and enhanced methane production, respectively. However, to the best of our knowledge, no study has been focused on the effects of waste iron addition on hydrogen sulfide (H_2S) reduction in biogas.

Hydrogen sulfide is present in biogas at concentration ranges from 10 to 10,000 μL/L, which varies depending on the composition of the feedstock and digester technology (Pipatmanomai et al., 2009; Rasi et al., 2011). It is a deleterious gas that has caused the death of people and livestock (Dai and Blanes-Vidal, 2013; Andriamanohiarisoamanana et al., 2015). In anaerobic digestion, H_2S damages gas pipes and generators through corrosion since H_2S is biologically converted to sulfuric acid by sulfur-oxidizing bacteria (e.g., *Thiobacillus*), or by sulfidation, in which H_2S reacts with metals (e.g., iron, copper and silver; Maizonnasse et al., 2013; Nielsen et al., 2005). Generally, the cost of damages is estimated to be around 10% of the total investment cost (Zhang et al., 2008). Therefore, abating H_2S in biogas system is of interest to reduce biogenic corrosion in the biogas plant.

Among the various metals, iron salts have been used widely in biogas plants to control H_2S, since they are less expensive and less toxic than other metals (Cirne et al., 2008). Usually, the iron salt is mixed with a supporting material and is contained in a separate unit following the biogas digester (Cirne et al., 2008; Cherosky and Li, 2013). However, in addition to the cost for the biogas purification unit, purchasing and recycling of used iron salt are the major problems. Therefore, the direct mixing of an iron with the AD feed stream would be an efficient alternative to minimize the biogas plant operating cost and to controlling the dissolved sulfide concentration and its associated problems (Zhang et al., 2008). As a matter of fact, Cirne et al. (2008) and Park and Novak (2013) have investigated the direct mixing of commercially available $FeCl_3$ with sludge. They found a significant reduction of H_2S concentration. Since waste iron powder from laser cutting machine is freely available, its use in anaerobic digestion is assumed to affect positively the digestion process and minimize H_2S concentration in biogas.

The objective of this study was to investigate the utilization of waste iron powder, generated during laser cutting machine, in anaerobic digestion. The study was carried out into two steps. In the first step, batch experiments were conducted to determine the impact of waste iron powder addition on H_2S concentration, digestion stability and kinetic parameters. In the second step, a bench experiment using semi-continuous stirred-tank reactor was conducted to determine the efficiency of waste iron powder utilization in anaerobic digestion when it is fed daily into anaerobic reactor. To obtain useful information for academic and practical applications, experimental and mathematical approaches were undertaken. If waste iron powder is effectively control H_2S emission and does not influence negatively methane yield, it is expected to be an alternative way to reduce the installation and running costs of a biogas system.

2. Materials and methods

2.1. Materials

In this study, waste iron powder was obtained from iron and steel industry that uses oxygen as active assist gas of laser cutting machine. During laser cutting process, spark of dust (i.e., waste iron powder) was produced and collected.

Dairy manure was the substrate used as it is largely available in Hokkaido, Japan, and is a potential source of biomass energy in the region (Yabe, 2013). Fresh dairy manure was collected from a barn located in the northern part of Hokkaido. The total solids content (TS) of the manure was adjusted to 9%, which is the actual TS applied to the biogas digester at the farm, with volatile solids (VS) to TS ratio of 0.82.

2.2. Experimental procedures

To determine the effects of waste iron powder addition on H_2S control and digestion performance, two sets of laboratory experiments were conducted; anaerobic digestion under batch and bench conditions. The main objective of batch experiments was to investigate the reduction of H_2S production and improvement of methane yield, and digestion stability by the addition of waste iron powder, while bench experiment was conducted to investigate the efficiency of waste iron powder to control hydrogen sulfide in semi-continuous stirred tank reactors.

2.2.1. Batch experiments

Two series of batch experiments were conducted simultaneously to investigate (1) the effect of waste iron powder on H_2S concentration and kinetic parameters and (2) the change of AD process parameters resulting from the addition of waste iron powder. In both experiments, seven concentrations of waste iron powder were tested; 0.0, 2.0, 3.0, 4.0, 8.0, 12.0, and 20.0 g/L.

In experiment I, seven treatments (one control digester and six test digesters) were tested using 1.0 L laboratory scale digesters, made from polypropylene, with working volume of 600 mL. Six hundred milliliter of dairy manure was prepared and mixed with waste iron powder before feeding into digesters (T1 ~ T6). Control test was conducted where only dairy manure was fed to digesters (T0). The digesters were sealed and kept in water bath at 38 °C for 48 days under anaerobic conditions. Details of experimental design and influent characteristics are illustrated in Table 1. During the incubation period, the digesters were agitated manually every day. Hydrogen sulfide was measured every two to four days using a portable gas detector and manual gas pump equipped with fast-response detector tubes (Andriamanohiarisoamanana et al., 2015). The biogas was collected in 2-L Tedlar® gas-sampling bags, and the volume was measured using a wet-drum gas meter. The gas composition was analyzed using a gas chromatograph (GC). The initial and final pH, TS, VS, volatile fatty acids (VFA), and total

Table 1
Experimental design and influent characteristics for the batch experiment.

	Waste iron powder		Dairy manure (g)	TS (%)	VS (%)	VS/TS	pH
	Conc. (g/L)	Added (g)					
T0	0	0.0	600	9.03	7.44	0.82	7.58
T1	2	1.2	600	9.19	7.43	0.81	7.75
T2	3	1.8	600	9.24	7.40	0.80	7.62
T3	4	2.5	600	9.29	7.29	0.79	7.65
T4	8	4.9	600	9.67	7.34	0.76	7.64
T5	12	7.4	600	10.17	7.44	0.73	7.61
T6	20	12.3	600	10.84	7.39	0.68	7.55