

# **Electrochemical Removal of Aqueous Sulfide from Swine Manure**

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## Abstract

Hydrogen sulfide ( $\text{H}_2\text{S}$ ) produced in swine manure pit storage is a safety hazard to both human and animals. An electrochemical treatment based on low carbon steel electrodes was developed to reduce aqueous sulfide and emitted  $\text{H}_2\text{S}$  concentration from manure storage. At the selected condition (Applied voltage = 0.7 V, immersed electrode surface area =  $19 \text{ cm}^2/\text{L}$ , initial sulfide concentration = 5 - 6 mM, operation temperature =  $19 \text{ }^\circ\text{C}$ ), the process achieved an average sulfide removal rate of  $2.60 \text{ mg S}^{2-}/(\text{cm}^2 \cdot \text{day})$  for the zero order kinetic model, and a rate coefficient of  $0.275 \text{ /day}$  for the 1<sup>st</sup> order kinetic model. Constant disturbance created to simulate the pumping event was found greatly accelerated the  $\text{H}_2\text{S}$  release directly from the manure liquid; however, removals of over 90% sulfide and  $\text{H}_2\text{S}$  significantly reduced the risk. Methane concentration went higher as the sulfide removal; 46% higher concentration was found at 95% sulfide removal from the initial concentration over 6 mM. Different from the electrochemical sulfide removal from less viscous wastewater, low voltage applied in this study was proved feasible to maximize the precipitation and minimize the flotation in swine manure. The installation of this technology may reduce the risk of manure pump-out in terms of  $\text{H}_2\text{S}$  over-exposure and may be applied in similar circumstances where  $\text{H}_2\text{S}$  poses threats to health and life.

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## Chapter 1: Background

### 1.1 H<sub>2</sub>S Issue in swine manure

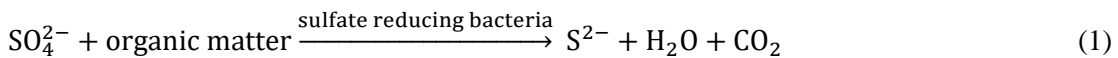
#### 1.1.1 Hydrogen sulfide as a hazard

The presence of hydrogen sulfide (H<sub>2</sub>S) during the swine manure storage can create hazardous and even dangerous environment for both humans and animals [1]. Symptoms of acute exposure to this gas include headache, irritation, conjunctivitis, pulmonary edema, etc., and can cause life-threatening situations if the gas concentration is above 500 ppm. The Immediately Dangerous to Life or Health (IDLH) given by the National Institute for Occupational Safety and Health (NIOSH) is 100 ppm, a concentration considered immediately dangerous to life. Nowadays, the installation of ventilation and timely evacuation can greatly reduce the risk of being overexposed to the gas, but casualties still happened when barn workers were handling swine manure [1-4].

H<sub>2</sub>S is also corrosive and flammable, as corrosion can always happen during the storage or gas transportation on metals, and explosion happens within the range of 4.5% to 45.5% in the air. In addition, the dissolved sulfide and H<sub>2</sub>S in liquid is toxic to methanogenesis, which is a key step during the anaerobic degradation, resulting a negative impact to the swine manure management as the fertilizer [5, 6].

#### 1.1.2 Safety risk during swine manure pumping

In the case of a swine barn, manure drops through the slatted floor where the pigs stand on, into a deep pit. The storage could last for a year until the pit is full and manure needs to be pumped out [7]. Swine manure in pit storage has lots of bacteria species, massive nutrients, a high moisture level, neutral pH and very limited amount of oxygen, therefore, it is an excellent place for bacteria to boom. The sulfate reducing bacteria (SRB) inside converts protein and sulfur-containing organic matter into H<sub>2</sub>S [2]. In the manure storage, hydrogen sulfide (H<sub>2</sub>S, pK<sub>a</sub> ≈ 7.0), bisulfide (HS<sup>-</sup>) and sulfide (S<sup>2-</sup>) can be converted to each other under different pH levels, and the complete generation process of H<sub>2</sub>S is shown in Eq. (1), (2) and (3) [8]:





Under a neutral or low pH level,  $\text{H}_2\text{S}$  is the dominant species; for instance, a pH drop from 7 to 6 increases the  $\text{H}_2\text{S}$  distribution level up to 90% from 50%, while at the pH of 8,  $\text{H}_2\text{S}$  only accounts for 10%.  $\text{HS}^-$  starts dominating between pH of 7 to 12, and  $\text{S}^{2-}$  only exists at alkaline conditions [8, 9]. Therefore, there could be a large  $\text{H}_2\text{S}$  emission potential in the swine manure storage. Especially in confined spaces like a barn, the emission of  $\text{H}_2\text{S}$  from swine manure contributes a significant safety hazard to the barn management.

During the manure storage with ventilation, the  $\text{H}_2\text{S}$  concentration can be kept below 1 ppm, depending on the season [10-12], temperature [13], and ventilation rate [14]. However, previous studies have pointed out a  $\text{H}_2\text{S}$  burst during the manure flowing. A sharp increase of  $\text{H}_2\text{S}$  level inside the barn was found as the turbulence of dairy and swine manure was increased during the mixing [15]. A study on the  $\text{H}_2\text{S}$  concentration at the pit, sidewall and tunnel of the swine barn reported an increase of  $\text{H}_2\text{S}$  emission by an average of 61.9 times during the slurry removal events with the corresponding  $\text{H}_2\text{S}$  concentration at 36 ppm at the highest [7].  $\text{H}_2\text{S}$  level increase can also happen during swine manure flushing, explained by the turbulence of manure caused by the strong water flow [16]. Moreover, a larger variance may exist in terms of the  $\text{H}_2\text{S}$  emission, a unpredictable  $\text{H}_2\text{S}$  level change pattern with the maximum reached beyond 1000 ppm was reported [11], illustrating that the peak  $\text{H}_2\text{S}$  concentration could reach over 10 times the IDLH.

It was concluded that the manure bottom layer had the highest potential to generate  $\text{H}_2\text{S}$  [17]. A bubble-release model was developed to explain the “ $\text{H}_2\text{S}$  burst-release” [18]. Small gas bubbles agglomerated to form large bubbles, which were capable to move upward to the manure surface. When an external force was applied, the disturbance caused a stronger bubble collision, therefore, gas bubbles were released at a faster rate.

Author concluded there could be two reasons for  $\text{H}_2\text{S}$  burst issue. One is the gas bubble breakage due to the manure movement, and the other one is the accelerated convection mass transfer due to the turbulence given by the constant agitation and pumping. In author’s opinion, in either way,  $\text{H}_2\text{S}$  mass transfer is bidirectional, meaning:

1.  $\text{H}_2\text{S}$  could travel back to the liquid phase if its concentration is lower compared to the equilibrium state; in the other words, although gas bubbles with high  $\text{H}_2\text{S}$  concentration

has been generated, a removal of aqueous sulfide from liquid phase can remove H<sub>2</sub>S in gas phase by inducing a backtrack.

2. The elimination of aqueous sulfide would reduce the H<sub>2</sub>S emission due to the convection mass transfer from liquid to the air.

## 1.2 Review of H<sub>2</sub>S removal

### 1.2.1 Gaseous stream removal

To eliminate H<sub>2</sub>S, previous researches can be classified into gaseous H<sub>2</sub>S removal and aqueous sulfide removal.

For gaseous H<sub>2</sub>S removal, a well-known technique is the Claus process, a traditional desulfurizing process that has been applied in natural gas and petroleum industry. Claus process is capable to remove a large amount of H<sub>2</sub>S in the inlet gas stream (greater than 15 vol%), and recover elemental sulfur [19]. The process contains a thermal step and an analytical step; the overall sulfur recover efficiency can reach more than 95%. Besides the Claus process, adsorption using activated carbon, biochar and zeolite have been widely studied [20-22]. Bio-filters, bio-trickling filters and bio-scrubber are microaerobic ways to remove H<sub>2</sub>S [23-25].

For all those techniques, a sufficient amount of retention time is required for H<sub>2</sub>S to contact with substrates. Considering the H<sub>2</sub>S burst that releases massive H<sub>2</sub>S at a short time, aqueous sulfide removal may turn out a more promising way to eliminate sulfide species in advance, and consequently lower the H<sub>2</sub>S emission.

### 1.2.2 Liquid stream removal

One of the most common dosing techniques to prevent the H<sub>2</sub>S generation is the aeration. By introducing oxygen into the waste stream, anaerobic metabolism can be prevented due to the increase of dissolved oxygen (DO). On the other hand, if sulfide has already been generated in wastewater, the presence of oxygen can oxidize the existed sulfide [26]. It was reported that by injecting oxygen at 15-25 mg/L into the sewer inlet, the sulfide discharge level was decreased by 65%, and the termination of aeration would bring a resumed sulfide production [27]. Nevertheless, aeration will not be a good solution to remove aqueous sulfide in manure storage

pit due to the inhibition oxygen can cause to the manure anaerobic condition, and the generation of gas bubbles should be minimized in case of being trapped inside the manure storage.

Similar to the aeration, strong oxidants also showed promising performances in aqueous sulfide removal, for example, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), sodium hypochlorite [28, 29]. The dosing of  $\text{H}_2\text{O}_2$  may cause the trapped gas bubble issue. Hypochlorite is known a common water sanitizer. Whether or not it has an impact to manure anaerobic degradation is not known, and the introduction of chlorite species may also cause unwanted environment issues.

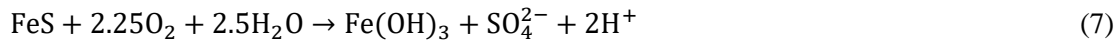
Dosing alkali is another convenient way to control the  $\text{H}_2\text{S}$  issue. As mentioned in 1.1.2 that the presence of  $\text{H}_2\text{S}$  drops significantly if the solvent is reaching alkaline. It was found that the dosing of alkali not only inhibited the  $\text{H}_2\text{S}$  emission, but also lowered the SRB activity [30]. In author's opinion, alkali dosing can slow down or terminate the manure anaerobic degradation process. The afterward pH adjustment to neutral may raise the  $\text{H}_2\text{S}$  issue again. Therefore, it is a temporary treatment rather than the long lasting one.

Biogenic ways to remove aqueous sulfide were also developed. By adding nitrate into wastewaters to promote the biological oxidation of sulfide, sulfide was found successfully decreased by 98.7% in the air, and 94.7% in liquid phase at a dosing amount of 0.18 mM and HRT = 3.5 hr [31]. Synergistic inhibition between nitrite and molybdate onto the SRB *Desulfovibrio* sp. Strain Lac6 from produced water was also studied, with a maximum dosing amount of 4 mM nitrite and 0.47 mM molybdate to suppress the sulfide production during the bacteria exponentially growth period [32]. Regarding the disadvantages, It was found that the dosing of nitrate can inhibit the methanogenesis just like the sulfide [33]; Nitrite was also found to be an inhibitor to methanogenesis [34, 35]. Therefore, the dosing of nitrate or nitrite may not perform well on substrates like manure, which requires a long-time degradation and methane as one of the energy products. In addition, nitrate can be reduced into nitrite; the application of nitrogen compounds may increase the risk of groundwater pollution. Considering those negative impacts, the dosing of nitrite or nitrate may not be suitable solutions.

Direct iron dosing is another technique that has been studied since an earlier time. Iron salts including ferrous chloride ( $\text{FeCl}_2$ ) and ferric chloride ( $\text{FeCl}_3$ ) were both proved to be effective in removing aqueous sulfide from the sewer. The removal mechanism was concluded in Eq. (4) and (5) [36, 37].



The main final product, ferric sulfide (FeS), has a black color that can be easily differentiated from non-treated groups. Although FeS has a low solubility under the neutral or alkaline conditions, it is acid soluble and can be oxidized. Equations concluded from previous studies are shown below [38, 39]:



Previous studies showed that a large negative ( $\leq 200$  mV) Oxidation/Reduction Potential (ORP) can accelerate the conversion to Fe (II) from Fe (III), along with the oxidation of sulfide; an anaerobic dosing of Fe(III) to completely form FeS rather than the aerobic dosing was suggested [40]. This finding made the iron dosing technique more suitable to be applied in swine barn because manure storage pit is highly oxygen limited.

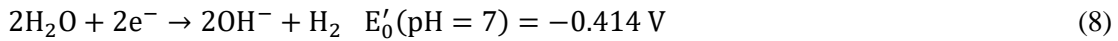
However, direct iron dosing has its disadvantages. The main disadvantage is that it brings in strong acidic ferric salts, which may lower the waste stream pH level, increasing the  $\text{H}_2\text{S}$  release potential and the ideal dosing amount [41-43]. It was reported that iron salts were very corrosive, and iron dosing becomes significantly less effective if the waste stream pH was below 6.5 [26]. Compared to wastewater, although manure has a neutral pH level around 7.0, the volatile fatty acid generation under the anaerobic condition may constantly decrease the pH level.

### 1.2.3 Electro-precipitation

In recent years, sulfide removal by electrochemical methods were widely studied in different liquid streams. It was concluded by Pikaar, electrochemical methods of sulfide abatement included anodic sulfide oxidation, electro-precipitation, which can also refer to electro-coagulation and electro-flotation, and caustic generation [44]. Different from the precipitation, flotation and caustic generation were contributed by cathode instead of anode, by the means of hydrogen/oxygen gas and hydroxide production.

In this study, electro-precipitation was the primary method to lower aqueous sulfide concentration. In the case of iron as the anode material, the cell reactions get involved are shown below [43]:

Cathode:



Anode:



The sulfide removal principle is similar but better than direct iron dosing. For electro-precipitation, when electrical current is passing through the electrodes, iron released from anode is consumed to form precipitate with any existing bisulfide; the precipitate generated is FeS. On cathode, hydroxide generated increases the stream pH level, representing a less potential of H<sub>2</sub>S emission. Previous studies showed that close or over 90% sulfide removal can be achieved by electrochemical methods in streams like sewage, tannery wastewater, paper mill wastewater and digested dairy manure, under relatively high applied voltages mostly beyond water electrolysis (1.23 V) [43, 45-47]. More than merely the sulfide, electro-precipitation showed strong removal efficiencies in oil, COD, suspended solids, heavy metal, color, and phosphorous etc. as well [48-53]. Hence, it was widely studied in the fields of wastewater treatment to separate or remove particular substance or elements. Besides iron, stainless steel and aluminum were typical electrode materials as well [54].

### 1.3 Application in Swine Manure Storage

Gas production (H<sub>2</sub> and possibly O<sub>2</sub>) from cathode contributes to the flotation, which provides an upward momentum and drive the suspended particles onto the stream surface [45]. However,



excess amount of gas generated could create void space in manure storage due to its high viscosity, decreasing the storage time. The presence of  $H_2$  may also increase the explosive concern, and  $O_2$  can inhibit the anaerobic bacteria growth. Therefore, gas generation is in parallel with hydroxide generation on cathode but less desired in the case of swine manure storage, with total solid content (TS) typically ranges from 2% to 6% [55]. It was concluded by Holt, regarding the turbidity, higher fraction was removed by flotation when the current density was relatively high [56]. In the other word, a higher weight of precipitation may occur when the power input was relatively low. To make this technique applicable in swine manure sulfide removal, a strong precipitation but a weak flotation is expected. From this perspective, sulfide removal from anode is favored and gas production from cathode can be minimized.

#### **1.4 Experimental hypothesis and purpose**

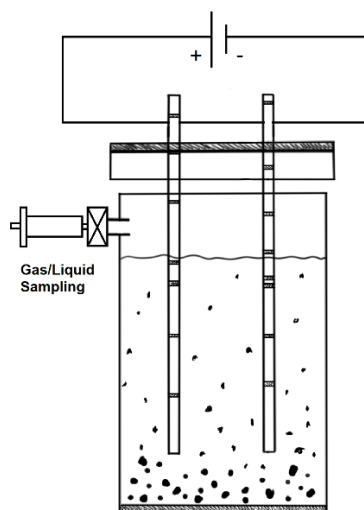
Considering the huge safety concern during the manure pumping event, and the advantages of electrochemical treatment has shown in the previous studies, author hypothesized that sulfide can be removed from swine manure storage under a low voltage below the water electrolysis level using stainless steel 304 and low carbon steel as the sacrificial electrodes. Various parameters regarding the electrochemical condition and manure storage condition were tested to understand the process characteristics. Simulation to the manure pumping/agitation was performed to examine the feasibility of using the electrochemical technique to solve the  $H_2S$  burst issue. Furthermore, concentration of methane production was examined to see the impact this technique can bring to the manure anaerobic degradation. It was expected that the technique consequently can solve not only the safety issue to animals and humans, but also provide a better manure anaerobic degradation environment.

## **Chapter 2: Material and Method**

### **2.1 Electrode material and reactor design**

500 ml polyethylene bottles (6FAH7, Grainger, Lake Forest, IL) were used as reactor vessels (Fig. 1). a 4-way stopcock with luer connection (EW-30600-09, Cole-Parmer, Vernon Hills, IL) was connected to the reactor vessel at 12.5 cm height above the reactor bottom, and a 12 ml syringe (8881512852, Covidien, Dublin, Republic of Ireland) was connect to the stopcock for gas

and liquid sampling. Reactors for control group did not have electrode except those involved in electrode area test (Fig. 3). For experiment group, low carbon steel (LCS) (9255T39, McMaster) and stainless steel 304 (SS 304) (9358T23, McMaster, Elmhurst, IL) was used as the electrode material, with 0.0762 cm thick and had 40% open area. Stainless steel was cut into 17.5 cm × 3.5 cm electrode pieces, while low carbon steel was cut into 17.5 cm × 0.7/1.4/2.1/2.8/3.5 cm pieces. An electrode pair was separated by Marine grade wood (5068K53, McMaster) at 1.905 cm distance; Strips-Balsa (1125T41, McMaster) was used additionally to mount electrode pairs. Each electrode pair was inserted through the reactor lid, with 3.5 cm length above the lid for the connection to the power, and 14.0 cm inside the reactor. Loctite® Epoxy Adhesive (1405602, Menards, Eau Claire, WI) was used to support the bonding of electrode pair onto the reactors lid and the stopcock. Surebonder Acrylic Adhesive (H-810R, Menards) was used additionally to seal the reactor to be air-tight. Electrodes of experiment reactors served as either anode or cathode by connecting to power supplies (CircuitSpecialists, Tempe, AZ).



**Fig. 1** – Experimental reactor design with electrode.

## 2.2 Manure preparation and sulfide dosing

Fresh swine manure was collected on the ground from Swine Research Facility in St. Paul, at University of Minnesota Twin Cities; it was mixed with tap water and stored at 4 °C for two weeks, then filtrated through a 2 mm opening size sieve (W.S. Tyler, Ohio). Coarse solids were not used, and the concentrated manure slurry was diluted into TSs of 0.2%, 1%, 2%, 4% and 6%

by tap water before being transferred into the reactors. 3 days to acclimate were allowed after the manure dilution. The volume of manure in each reactor was  $400 \pm 10$  ml, with 100 ml headspace. The headspace was flushed by nitrogen gas before the being capped by the reactor lid.

Reactors with manure being transferred were placed under room temperature for one week to ensure a relatively stable anaerobic condition was achieved. Then, 200 g/L external concentrated sodium sulfide solution, prepared from sodium sulfide nonahydrate ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) (387065000, Acros Organics, Waltham, MA), was injected into the reactor by syringe to increase the initial manure liquid sulfide concentration. The first day of the measurement, recorded as “Day 0” started 3 days after the sulfide injection to allow the equilibrating process of  $\text{H}_2\text{S}$  transferred from manure liquid to reactor headspace.

## **2.3 Chemical analysis**

### **2.3.1 Liquid analysis**

Involved reactors were mixed by manually turning upside down for 3 times before each sampling. 2 ml liquid sample was taken each time for sulfide analysis. At the first and last sampling day, 6 ml extra amount of liquid sample was taken for other analyses.

pH, conductivity and Oxidation/Reduction Potential (ORP) were measured by using corresponded meters (Cole-Parmer, Illinois).

Total phosphate and Chemical Oxygen Demand (COD) were measured by Hach kits (TNT 845 and TNT 823, Hach, Loveland, CO).

Sulfide concentration was measured according to the Standard Methods for the Examination of Water and Wastewater [57]. In this study, sulfide can be measured in water, raw manure, manure supernatant and manure solid. 7000 rpm for 10 min centrifugation was applied on raw manure to obtain the manure supernatant and manure solid. Manure solid was taken at the same volume as other liquid samples for the sulfide measurement. To eliminate the impact by solid in manure in the sulfide measurement, the mixture solution with manure and Sulfide Anti-Oxidant Buffer was centrifuged at 7000 rpm for 10 min to remove solids. Then supernatant was taken and measured by Silver/Sulfide ISE Electrode (27502-41, Cole-Parmer).

For sulfate analysis, the diluted manure sample was centrifuged at 13,000 rpm for 3 min. The supernatant was then passed through the 0.45  $\mu\text{m}$  nylon filter (F2500-1, Fisher Scientific, Hampton, NH) before loaded into an ion chromatograph (IC) for measurement. Sulfate concentration was determined with a Dionex 2100 anion system equipped with an Ionpack AS19-RFIC 2 x 50 mm column with an AG19 RFIC guard column and an AERS 500 suppressor. The eluent is 20 mM KOH at a flow rate of 0.25 ml min<sup>-1</sup>. Samples were injected with a direct auto-sampling device, model AS-DV. All aspects of the Ion Chromatography device were controlled by the Chromeleon 7 software.

### 2.3.2 Gas Composition Analysis

10 ml of gas sample was taken from the reactor headspace for gas composition analysis. As the compensation to the internal pressure, 10 ml nitrogen gas was injected into the after each gas sampling.

Gas sample was analyzed via gas chromatograph (GC) (CP-4900 Micro-GC, Varian Inc., Palo Alto, CA). The GC had two columns set up with molecular sieve 5A and Porapak Q. Helium was used as the carrier gas. The temperatures for the sampling line, the injector, and columns were set at 50, 110, and 80 °C, respectively. Gas components were determined with a thermal conductivity detector (TCD) in the micro-GC. H<sub>2</sub>S concentrations in the biogas samples were determined using RAE Systems H<sub>2</sub>S tubes of varying testing ranges based on the real concentration, expressed in ppm by volume [47].

### 2.3.3 Current density monitoring

A CR1000 data logger with a multiplexer (Campbell Scientific, Inc., Logan, UT) was used to read the voltage across an 8.2  $\Omega$  resistor (Resistor Kits, Joe Knows Electronics). Readings were taken and recorded that was in series with the target reactor every 1 minutes over the entire process. Current density was calculated by dividing the monitored voltage by the product of resistor (8.2  $\Omega$ ) and immersed area of a single piece of electrode.

### 2.3.4 Statistical analysis

The kinetic analysis (zero and 1<sup>st</sup> order) was done in Excel via Add Trendline option. Regression analysis was done in Excel via Data Analysis add-in. Confidence level was set as the default value of 95%. Results were analyzed in percentage-based sulfide removal.

## 2.4 Exploration experiments design

### 2.4.1 Manure solid interference test

Ten 500 ml reactors were prepared and randomly assigned, with two filled with 400 ml DI water and others filled with 400 ml swine manure with TS of 1%, 2%, 4% and 6%, replicates = 2. 200 g/L Na<sub>2</sub>S·9H<sub>2</sub>O concentrated solution was consecutively pipetted into each bottle with accumulated amounts of 0.2, 0.5, 1, 2, 4, 6 and 8 ml. All reactors were manually mixed by turning upside down for 6 times and 5 ml samples were taken to measure sulfide concentrations after each sulfide addition. Different from other tests involved in this study, centrifugation at 7000 rpm, 10 min was not applied in this test for sulfide measurement. Due to the possible reading fluctuation involved in this test brought by the manure TS, the reading stayed the longest time (over 5s) were taken, read by Silver/Sulfide ISE Electrode (27502-41, Cole-Parmer). All the sulfide concentrations measured at different dosing amount with different manure TS were compared to the DI water results. The test was done at room temperature (19 ± 1 °C). The measure difference between manure samples and DI water samples was calculated as:

$$\text{Fraction from the DI water samples \%} = \frac{\text{sulfide(aq) measured in manure samples}}{\text{sulfide(aq) measured in DI water samples}} \quad (9)$$

### 2.4.2 Analysis of sulfide distribution in swine manure

72 samples were randomly taken from the reactors with TS 2% swine manure. Those reactors were from the preliminary studies with different amount of sulfide concentrations. Raw manure, manure supernatant and manure solid samples were all analyzed from those reactors. The test was done at room temperature (19 ± 1 °C). The difference between the raw manure and manure solid was calculated as:

$$\text{Difference \%} = \frac{\text{sulfide(aq) in raw manure} - \text{sulfide(aq) in manure solid}}{\text{sulfide(aq) in raw manure}} \quad (10)$$

### 2.4.3 Stainless steel (SS) 304 as the electrode

Stainless steel 304 was the first material used for sulfide removal. Voltage was examined to see the electrochemical removal feasibility; applied voltages included 0 V (control), 0.8V, 1.2 V, 1.6 V; besides, a group of 3.0 V was prepared to examine the liquid and solid separation under a relatively high applied voltage. In total, 5 conditions with three replicates were prepared. The electrode area used was 95 cm<sup>2</sup>/L; TS was controlled to be 2%. The test was done at room temperature (19 ± 1 °C). Initial sulfide concentration was increased to around 3 mM. 3 days were allowed for the equivalent process of sulfide species. Sampling time were 0, 46, 88, 132, 201 and 270 hr.

## 2.5 Central composite experiment design

### 2.5.1 Parameter conditions

Low carbon steel was used as the only electrode material. Variables involving applied voltage, electrode surface area (ratios to medium volume, immersed part), manure TS, initial sulfide concentration and operation temperature were analyzed. Table 1 shows the central condition selected, indicating the condition selected when one of the parameters is serving as the test variable. All conditions had a replicate of 3.

**Table 1** – Central condition concluded from deduction of possible parameters.

<b>Voltage applied</b>	0.7 ± 0.02 V
<b>Immersed electrode surface area per pair</b>	19 cm <sup>2</sup> /L [a]
<b>TS</b>	2 ± 0.1 %
<b>Initial sulfide level</b>	Around 6 mM
<b>Operation temperature</b>	19 ± 1 °C

[a] Calculated by 2 × 9 cm (fixed) × 0.7 cm (variable) × 0.6 (porosity) ÷ 0.4 L (reactor volume)

### 2.5.2 Effect of electrochemical parameters

In the test on optimal applied voltage, a control group without electrode was involved, in experimental groups, applied voltages of 0.3 V, 0.5 V, 0.7 V and 1.0 V were constantly applied on the reactors. Manure samples were taken at day 0, 1, 3, 15 for analysis.

In the test on electrode contact area, a control group without electrode was involved, the immersed electrode area in experimental groups were 95/76/57/38/19 cm<sup>2</sup>/L. Sampling days were 0, 3, 6 and 9.

### 2.5.3 Effect of waste storage conditions

In the test on manure solid content, two control groups without electrode, with the TS of the lowest (0.2%) and the highest (6%) were involved. Manure liquids with TS of 0.2%, 1%, 2%, 4%, 6% were involved in experimental groups with electrochemical treatment. Sampling days were 0, 3, 6, and 9.

In the test on initial sulfide concentration, two control groups without electrode, with the lowest initial sulfide concentration of 2 mM and the highest of 8 mM were involved. The initial sulfide concentrations in experimental group were 2, 3, 5 and 8 mM in experimental groups with electrochemical treatment. Sampling days were 0, 3, 6, 9, 12 and 18. Headspace gas composition concentrations were measured by GC.

In the test on operation temperature, three control groups without electrode, with the operation temperature of  $4 \pm 1^\circ\text{C}$ ,  $19 \pm 1^\circ\text{C}$  and  $31 \pm 1^\circ\text{C}$  were involved. Another three groups at same temperatures served as experimental groups with electrochemical treatment. Samples days were 0, 3, 6 and 9. Headspace gas composition concentrations were measured by GC.

### 2.5.4 Manure management simulation test

For manure management simulation test, low carbon steel was used as the only electrode material. 9 control reactors without electrode and 9 experimental reactors with electrode under constantly applied voltage were studied at the central condition. At day 3, 6 and 9, 3 reactors were randomly chosen and sampled from control and experimental groups, respectively. Involved reactors were mixed by manually turning upside down 3 times before sampling. After taking the liquid and gas samples, reactor headspaces were flushed by N<sub>2</sub> and capped again, then reactors

were transferred onto a shaker at 210 rpm for 20 min. After shaking, the H<sub>2</sub>S concentrations in reactor headspace were measured at the second time. Served as control to the shaking simulation, another 3 reactors were tested following the same steps, except that those reactors were not loaded onto the shaker during the 20 min. The purpose of the simulation test was to create a H<sub>2</sub>S rich environment under a turbulent liquid condition to represent manure pit pumping/agitation prior to emptying. The gas recovery (e.g. H<sub>2</sub>S and methane) in this study can be calculated by dividing the headspace concentration after 20 min shaking/non-shaking by the concentration measured after manually mixing.

## **2.6 Extension study**

### **2.6.1 Sterilization & Non-sterilization test**

Low carbon steel was used as the electrode material. 4 conditions were involved a replicate of 3; they were evenly divided into sterilization and non-sterilization groups. For each group, one condition without electrode served as control, and the other with electrochemical treatment served as experimental reactors. Reactors from sterilization group were autoclaved for 60 min at 104 °C (220 °F), while for non-sterilized reactors, raw swine manure was added. The test followed central condition; sampling happened on day 0, 3, 6 and 9.

### **2.6.2 Sulfide removal potential test**

Low carbon steel was used as the electrode material. 12 Reactors from manure management simulation test were randomly selected after 9 days electrochemical treatment period. Given a 24 days experimental period, applied voltage was continued on those reactors for 0, 6, 12 and 24 days, with a replicate of 3, while the power was shut down during other days. At day 24, 200 g/L external Na<sub>2</sub>S·9H<sub>2</sub>O concentrated solution was injected to all reactors at concentrations about 3 mM S<sup>2-</sup>, 3 days was given to allow the equilibrating process of H<sub>2</sub>S transferred from manure liquid to reactor headspace. Both S<sup>2-</sup> and H<sub>2</sub>S were measured before and after the external sulfide dosing. The test was done at room temperature (19 ± 1 °C).

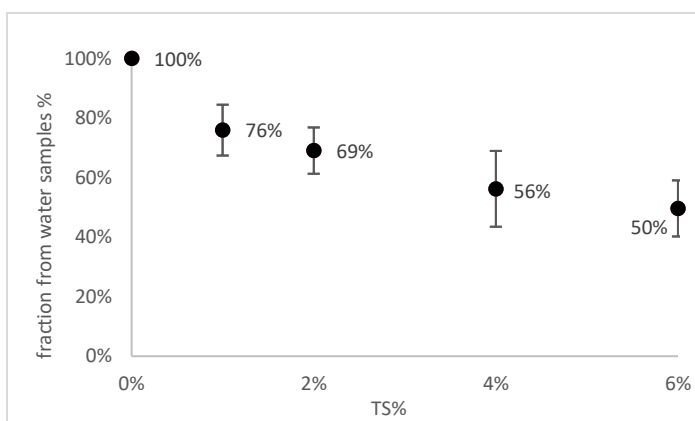
## **Chapter 3: Results and Discussion**



### 3.1 Exploration experiments

#### 3.1.1 Manure solid interference

The manure initial sulfide concentrations were 1.8 mg/L, 2.3 mg/L, 6.5 mg/L and 9.7 mg/L for TS of 1%, 2%, 4% and 6%, respectively; they were subtracted from the total sulfide concentrations measured during the analysis. Shown in Fig. 2, set the water as the ideal condition without any impact brought by TS, the fraction of water was 1. As the TS in swine manure increased, the actual aqueous sulfide concentrations measured were becoming significantly lower comparing to the actual dosing amount. For TS of 1%, 24% aqueous sulfide was not detected by the probe; if the TS is increased to 6%, 50% of the aqueous sulfide was not detected. The low p-value (0.0000) also illustrated that manure solid content cause inaccurate probe measurements.



**Fig. 2** – Aqueous sulfide concentration comparison between swine manure at different total solid contents and DI water at the same dosing amounts.

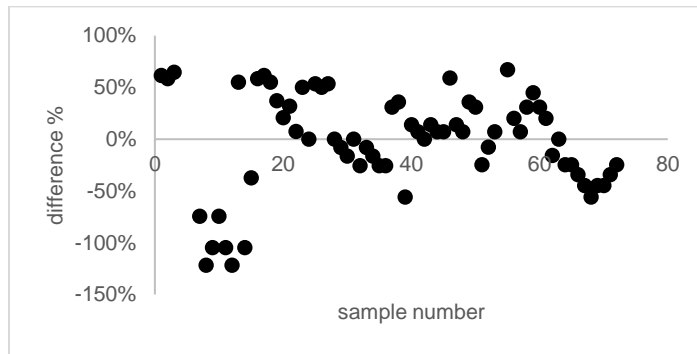
One explanation to this observation was that the TS could affect the water activity. The change of water activity furtherly created an inhibition to the sulfide ion activity detected by the probe; therefore, an inaccurate reading happened that could cause misleading results. The importance of this experiment was that it discovered an issue that TS can bring in the sulfide measurement. The inaccuracy brought by manure TS suggested that a separation step was needed before taking the sulfide probe readings. Later in this experiment, centrifugation at 7000 rpm for 10 min was done before the probe measurement was confirmed to be a suitable method to remove the manure TS impact; sulfide concentration reading was taken from the supernatant after the centrifugation.

#### 3.1.2 Sulfide distribution in swine manure

Knowing the importance of centrifugation, the aqueous sulfide distribution was investigated in the raw mixture, supernatant and solid. Concerns below were solved to prove the feasibility of centrifugation:

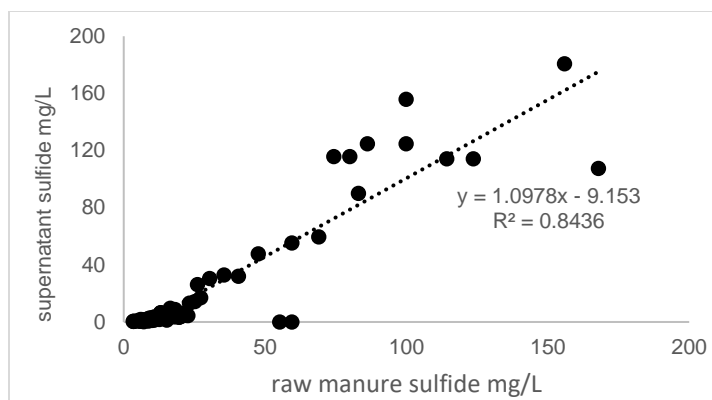
1. If more sulfide was found in manure solids than the supernatant, the sulfide reading by probe may still be lower than the expectation
2. If the manure solids can retain aqueous sulfide from being precipitated, the electrochemical treatment may be less effective to the overall sulfide concentration in manure

As shown in Fig. 3, the aqueous sulfide concentration difference between raw manure and manure solids is arranged around the x-axis (0% difference); points locate on both sides of the axis. By taking the average of all the points, 0.8% turned out to be the average difference. The high p-value (0.5506) suggested a weak evidence to indicate sulfide in raw manure was higher than manure solid on average. Therefore, aqueous sulfide in manure may have a homogeneous distribution in swine manure.



**Fig. 3** – Aqueous sulfide difference in percentage between the raw manure and manure solid.

Refer to Fig. 4. Supernatant sulfide increased as the raw manure sulfide. A trendline slope of 1.0978 indicated that the aqueous sulfide was nearly equivalently found in manure supernatant compare to that of the raw manure.



**Fig. 4** – Aqueous sulfide relationship between supernatant and raw manure.

By furtherly looking at all the aqueous sulfide concentrations, the minimum amount for manure supernatant was 0.05 mg/L, by contrast, for manure solid, the minimum was 3.82 mg/L. Therefore, sulfide in liquid can be reduced to a low level; however, a small amount of sulfide attached to, or retained in manure solids may not be easily removed. The explanations to this finding were:

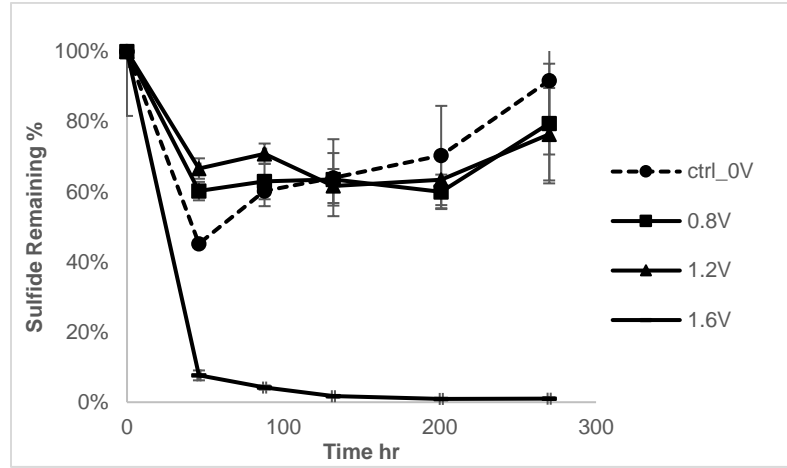
1. Swine manure solids may prevent sulfide from diffusing into the manure liquid
2. Due to the possible structure characteristics of swine manure solids, the iron ion coming from the anode may not be successfully delivered into the solid inside; hence, sulfide remained in aqueous form rather than being precipitated

Overall, results indicated that the sulfide contained in swine manure solids will not constitute a large interference to the sulfide measurement. A centrifugation pretreatment at 7000 rpm for 10 min was proven to be feasible to improve the data quality.

### 3.1.3 Stainless steel (SS) 304 as the electrode

Refer to Fig. 5 and Table 2, in the graph, “Sulfide Remaining %” indicates the percentage on average of the sulfide concentrations measured at certain day to the sulfide concentrations at day 0; reactors served as control without electrochemical treatment were indicated by “ctrl” while others were experimental groups (“exp”) with electrochemical treatment (applied voltages). For voltages of 0.8 V and 1.2 V, significant removals were not observed (p values > 0.05). When the applied voltage reached 1.6 V, 92% (41 mg/L) sulfide was removed within 46 h. At 270 h of 1.6 V, and the final sulfide removal was 99% (not shown in the table). The corresponding pH level

increased to 9.48 and became stable since 88 h, when 96% of the sulfide had been removed; the final pH was 9.36 at 270 h. Different from other groups, the swine manure conductivity at 1.6 V was found decreasing over time, at 88 h, the conductivity was 6.84, and it became stable to the end, with a final level of 6.68 at 270 hr. For those groups that sulfide was not successfully removed, the pH and conductivity patterns were similar; pH tended to decrease slightly, and conductivity tended to increase.



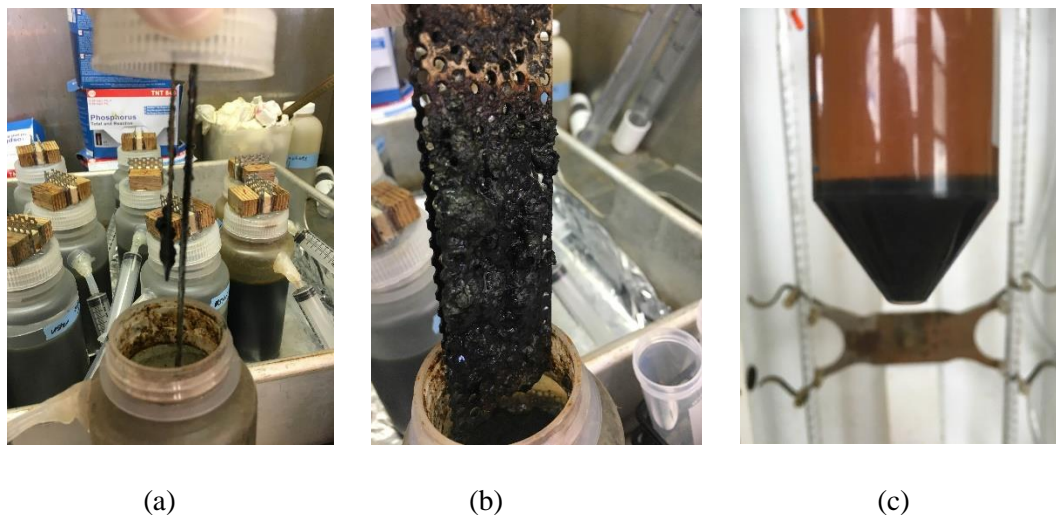
**Fig. 5** – Aqueous sulfide removal under different applied voltages using stainless steel 304 electrodes (Immersed electrode surface area =  $95 \text{ cm}^2/\text{L}$ , TS =  $2 \pm 0.1\%$ , operation temperature =  $19 \pm 1 \text{ }^\circ\text{C}$ , initial sulfide concentration =  $76 \pm 13 \text{ mg/L}$ , initial pH =  $6.94 \pm 0.03$ , initial conductivity =  $8.59 \pm 0.04 \text{ ms}$ ).

**Table 2** – Stainless steel 304 voltage test initial and final conditions.

Applied voltage (V)	initial sulfide (mg/L)	Treatment time (hr)	Initial pH	initial conductivity (mS/cm)	final pH	Final conductivity (mS/cm)	Sulfide Remaining (mg/L)
Ctrl	$93 \pm 17$	270	$6.91 \pm 0.01$	$8.59 \pm 0.07$	$6.60 \pm 0.3$	$11.22 \pm 0.03$	$85 \pm 20$
0.8	$73 \pm 3$	270	$6.92 \pm 0.1$	$8.61 \pm 0.07$	$6.61 \pm 0.01$	$11.09 \pm 0.06$	$58 \pm 13$
1.2	$72 \pm 3$	270	$6.95 \pm 0.01$	$8.58 \pm 0.05$	$6.60 \pm 0.02$	$11.01 \pm 0.03$	$55 \pm 9$
1.6	$66 \pm 3$	46	$6.96 \pm 0.05$	$8.59 \pm 0.02$	$9.00 \pm 0.27$	$7.57 \pm 0.41$	$5 \pm 1$

The increase of the pH level can be understood as the releasing of hydroxide group; the decrease of conductivity may due to the removal of some ions [52]. Consumption on the electrode surface was observed, illustrated a sacrifice of the electrode material to remove the aqueous sulfide and other components, shown in Fig. 6 (a)(b). An example of complete liquid and solid separation is shown in Fig. 6 (c), this was the case when the applied voltage reached 3.0 V. There

was no visible solid particle observed in the supernatant, which showed an orange color, representing an excess releasing of iron. The COD level was found 55% lower ( $15453 \pm 620$  mg/L) than the original swine manure ( $35080 \pm 4295$  mg/L). By contrast, for the bottom solid, after the mixture liquid was taken into the measurement, the COD level was 46% higher ( $52100 \pm 9457$  mg/L) than the original swine manure. For the reactive phosphate, 100% was removed from supernatant, while similar amounts were found in the bottom solid ( $599 \pm 173$  mg/L) compared to the original swine manure ( $582 \pm 118$  mg/L).



**Fig. 6** – Aqueous sulfide removal by stainless steel 304. (a) Consumption of anode. (b) sediments on anode. (c) solid and liquid separation; orange supernatant.

There were reasons why stainless steel 304 was not chosen as the final electrode material. First was the high voltage demand, meaning a higher electricity requirement. Second, the high voltage applied (1.6 V) went beyond the water electrolysis voltage (1.23 V), therefore, lots of oxygen and hydrogen could be generated; those gases may get trapped inside the manure storage, generating void space. Hydrogen and oxygen may bring a high risk of explosion, and the presence of oxygen can inhibit the anaerobic process. Finally, chromium, with an amount over 12% in SS 304 can also be released from anode along with the iron [58], raising another environmental issue.

### 3.2 Central composite experiment

#### 3.2.1 Effect of electrochemical parameters

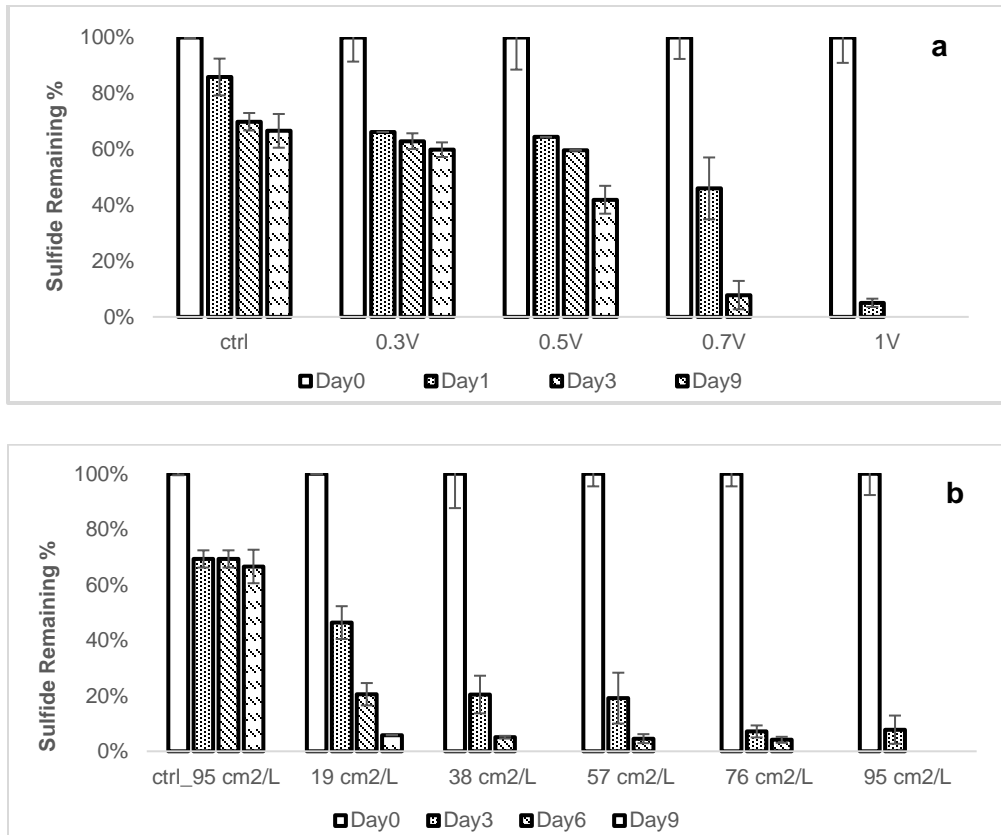
Fig. 7a and Table 3 show the sulfide removal efficiency in percentage under different applied voltages. Substantial removals were found in voltage of 1.0 V for 95% (206 mg/L) removal within 1 day, and 0.7 V for 92% (176 mg/L) removal in 3 days. A darker liquid color developed for both treatments, indicating the formation of FeS. Voltages at or below 0.5 V did not substantially remove sulfide over the experiment period (P values > 0.05 for all data from 0.3 V and day 3 and 6 data from 0.5 V). Overall, a higher voltage indicated a faster sulfide removal.

Considering both the sulfide removal and production of H<sub>2</sub>, 0.7 V turned out to be a suitable voltage. Paired with a 90% removal of sulfide, H<sub>2</sub> concentrations were  $43.32 \pm 8.58$  % and  $0.18 \pm 0.23$  %, for 1.0 V and 0.7 V, respectively. The gas productions were  $91 \pm 19$  ml and  $4.33 \pm 0.47$  ml, respectively. The higher H<sub>2</sub> concentration and greater gas production at 1.0 V indicated a stronger flotation rather than precipitation. Conversely, a higher weight of precipitation happened at 0.7 V. The finding from the sulfide removal standpoint was consistent with the study by Holt et al. from the view of turbidity [56]. 1.0 V was not considered an ideal applied voltage due to the management and safety concern it may rise.

After 9 days, pH of the control (“ctrl”), reactors with applied voltage of 0.3 V, 0.5 V, 0.7 V and 1.0 V changed to  $7.07 \pm 0.02$ ,  $6.50 \pm 0.02$ ,  $6.51 \pm 0.01$ ,  $6.51 \pm 0.03$ ,  $6.85 \pm 0.07$  and  $7.71 \pm 0.38$ , respectively. The change in pH as applied voltage demonstrated that paired with sulfide removal from anode, hydroxide generated from cathode can offset the pH drop brought by manure degradation and the sulfide precipitation from iron. As the power input increase, more hydroxide can be generated.

A clear pattern of the relationship between sulfide removal and electrode surface area was shown in Fig. 7b and Table 3, A higher sulfide removal can be achieved by increasing the electrode area (P value < 0.05). At  $95 \text{ cm}^2/\text{L}$ , 3 days was needed to remove 92% (176 mg/L) of sulfide, while for  $19 \text{ cm}^2/\text{L}$ , 9 days were needed to remove 94% (181 mg/L) of sulfide. When an acceptable removal efficiency was achieved, a smaller electrode contact area was preferred to reduce the capital cost of this technique.

At day 6, pH of reactors with electrode surface area of  $38 \text{ cm}^2/\text{L}$ ,  $57 \text{ cm}^2/\text{L}$  and  $76 \text{ cm}^2/\text{L}$ , changed to  $6.98 \pm 0.08$ ,  $7.16 \pm 0.25$  and  $7.59 \pm 0.14$ , respectively, indicating that a larger electrode surface area favored the hydroxide generation.



**Fig. 7** – Effects of electrochemical parameters, low carbon steel as electrode. (a) Under different applied voltages. (Immersed electrode surface area = 95 cm<sup>2</sup>/L, TS = 2 ± 0.1%, operation temperature = 19 ± 1 °C, initial sulfide concentration = 213 ± 31 mg/L, initial pH = 7.08 ± 0.05, initial conductivity = 5.23 ± 0.07 mS/cm); (b) Under different ratios of electrode surface area to medium volume. (Applied voltage = 0.7 V, TS = 2 ± 0.1%, operation temperature = 19 ± 1 °C, initial sulfide concentration = 196 ± 20 mg/L, initial pH = 7.18 ± 0.04, initial conductivity = 5.22 ± 0.11 mS/cm).

**Table 3** – Initial and final conditions in electrochemical parameter effects.

	Variable value	Initial sulfide (mg/L)	Initial pH	Initial conductivity (mS/cm)	Time (day)	Final pH	Final conductivity (mS/cm)	Final sulfide (mg/L)
<b>Applied voltage (V)</b>	Ctrl	191 ± 0	7.06 ± 0.04	5.19 ± 0.09	9	6.50 ± 0.02	6.61 ± 0.07	127 ± 12
	0.3	212 ± 18	7.09 ± 0.08	5.18 ± 0.05	9	6.51 ± 0.01	6.68 ± 0.1	127 ± 6
	0.5	218 ± 25	7.14 ± 0.02	5.27 ± 0.04	9	6.51 ± 0.03	6.68 ± 0.01	91 ± 11
	0.7	191 ± 15	7.07 ± 0.02	5.22 ± 0.04	3	6.85 ± 0.07	5.48 ± 0.04	15 ± 10
	1.0	217 ± 20	7.07 ± 0.01	5.28 ± 0.07	1	7.71 ± 0.38	5.36 ± 0.22	11 ± 3
<b>Electrode contact area per</b>	Ctrl	191 ± 0	7.06 ± 0.04	5.19 ± 0.09	9	6.50 ± 0.02	6.61 ± 0.07	127 ± 12
	19	192 ± 0	7.17 ± 0.01	5.12 ± 0.02	9	6.37 ± 0.02	6.17 ± 0.07	11 ± 0
	38	183 ± 23	7.18 ± 0.05	5.14 ± 0.08	6	6.98 ± 0.08	5.85 ± 0.08	9 ± 1

<b>pair</b>	57	187 ± 8	7.19 ± 0.04	5.33 ± 0.06	6	7.16 ± 0.25	5.81 ± 0.09	9 ± 3
<b>(cm<sup>2</sup>/L)</b>	76	203 ± 9	7.19 ± 0.07	5.28 ± 0.06	6	7.59 ± 0.14	5.73 ± 0.07	8 ± 2
	95	191 ± 15	7.07 ± 0.02	5.22 ± 0.04	3	6.85 ± 0.07	5.48 ± 0.04	15 ± 10

### 3.2.2 Effect of waste storage conditions

Shown in the Fig. 8a Table 4, for TS levels of 0.2%, 1%, 2%, 4% and 6%, sulfide removal efficiencies of 62% (125 mg/L), 93% (218 mg/L), 94% (181 mg/L), 96% (166 mg/L) and 92% (150 mg/L) were observed in 9 days treatment. Excluding results from 0.2% TS, P values over 0.05 indicated that a manure up to 6% of TS did not significantly affect the process efficiency.

At the TS of 0.2%, less amount of sulfide was removed, which was probably due to the high initial pH (above 10) and low conductivity. Regarding the pH effect, one possibility was that the higher pH slowed down the cathode reaction due to higher hydroxide concentration. Another possibility can be explained that under an alkaline condition,  $\text{Fe}(\text{OH})_4^-$  ion was formed rather than Fe(III) and Fe(II) [59]; therefore, sulfide was less likely to be precipitated during the electrochemical process. Regarding the conductivity, knowing a lower ohmic loss and higher current density can be achieved during electrochemical treatment at a high conductivity [59], TS of 0.2% might not be an efficient process due to its low conductivity compared to others.

Conductivity was found increased as manure TS (thickness); over 4 mS/cm conductivity can be observed for 1% TS and it reached over 10 mS/cm at 6% TS. Despite the higher thickness brought by solids may cause a limitation to the applied voltage, manure can have a much higher conductivity compared to many types of wastewaters with that of around 1 mS/cm [50, 60], indicating a more efficient electrochemical process.

As illustrated by Fig. 8b and Table 4, at day 6, 81% (48 mg/L), 87% (92 mg/L), 79% (139 mg/L) and 59% (170 mg/L) of sulfide removal were found from 2 mM, 3 mM, 5 mM and 8 mM initial sulfide concentration experimental groups, respectively. The final sulfide concentrations were all below 15 mg/L. A higher initial sulfide concentration indicated a slower removal by percentage (P value < 0.05); however, the removal rate by amount was found to be significantly higher as the initial sulfide concentration went higher.

A kinetic analysis involving the zero and 1<sup>st</sup> order was done based on experimental groups of 5 mM and 8 mM due to the sufficient points; points from the last measurement day were excluded from analysis. Trendline equations are shown in Table 5:



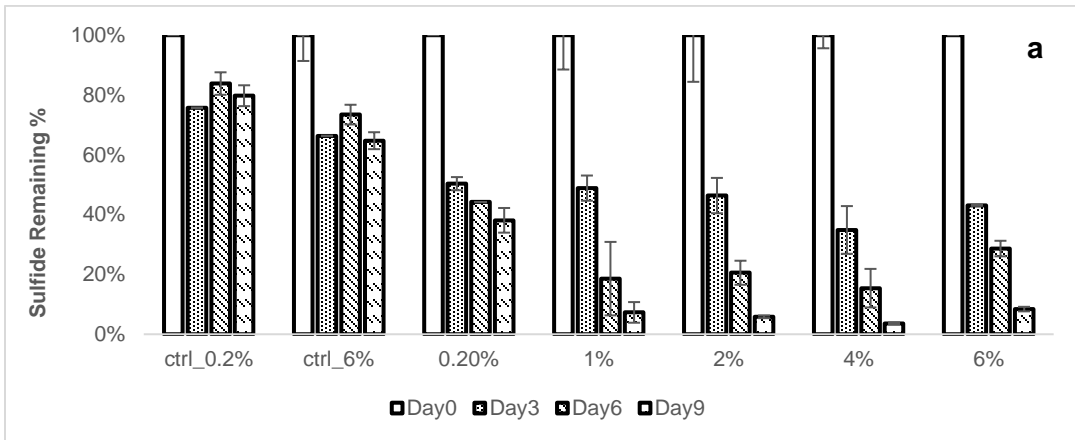
**Table 5** – Kinetic analysis in initial sulfide concentration test.

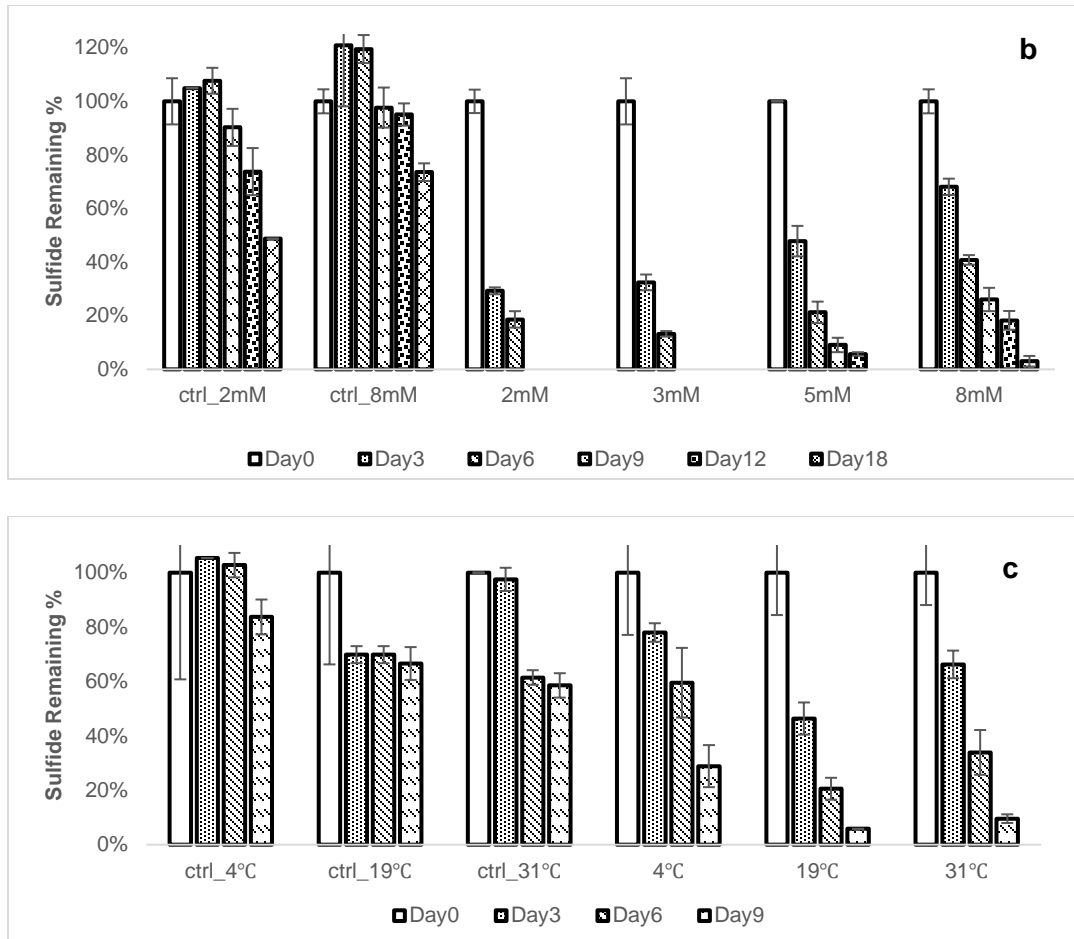
Initial sulfide concentration	Zero order	1 <sup>st</sup> order
5 mM	$S = -18 \cdot t + 158$ $R^2 = 0.917$	$S = 182e^{-0.267 \cdot t}$ $R^2 = 0.999$
8 mM	$S = -20 \cdot t + 264$ $R^2 = 0.941$	$S = 289e^{-0.145 \cdot t}$ $R^2 = 0.997$

\* S: sulfide remaining in manure in mg; t: electrochemical treatment time in day

The higher  $R^2$  may indicate that the process followed 1<sup>st</sup> kinetics, with the magnitude of rate coefficient decreasing as the initial sulfide concentration went higher. In author's opinion, the fit of zero order kinetic was acceptable to give a rough estimation of the process overall removal efficiency.

Shown in Fig. 8c and Table 4, the sulfide removal during the 9 days treatment were 71% (170 mg/L  $S^{2-}$ ), 94% (181 mg/L  $S^{2-}$ ) and 90% (192 mg/L  $S^{2-}$ ) at 4 °C, 19 °C and 31 °C respectively. P values above 0.05 indicated that temperature did not significantly affect the process.





**Fig. 8** – Effects of waste storage conditions, low carbon steel as electrode. (a) Under different swine manure TS. (Applied voltage = 0.7 V, immersed electrode surface area = 19 cm<sup>2</sup>/L, operation temperature = 19 ± 1°C, initial sulfide concentration = 192 ± 26 mg/L); (b) Under different initial sulfide concentration. (Applied voltage = 0.7 V, immersed electrode surface area = 19 cm<sup>2</sup>/L, TS = 2 ± 0.1%, operation temperature = 19 ± 1°C); (c) Under different operation temperatures. (Applied voltage = 0.7 V, immersed electrode surface area = 19 cm<sup>2</sup>/L, TS = 2 ± 0.1%, initial sulfide concentration = 201 ± 60 mg/L, initial pH = 7.49 ± 0.1, initial conductivity = 3.94 ± 0.07 mS/cm).

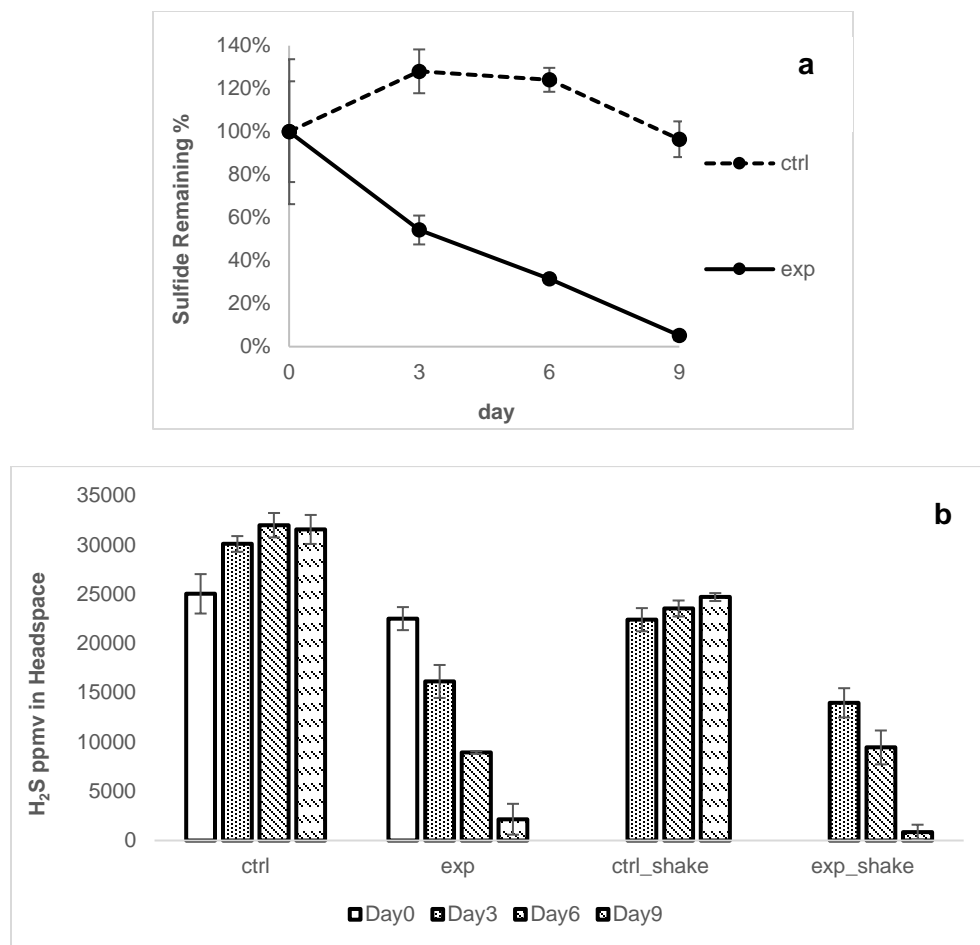
**Table 4** – Initial and final conditions in waste storage condition effects.

	Variable value	Initial sulfide (mg/L)	Initial pH	Initial conductivity (mS/cm)	Time (day)	Final pH	Final conductivity (mS/cm)	Final sulfide (mg/L)
<b>TS (%)</b>	Ctrl (0.2)	200 ± 0	9.57 ± 0.14	1.53 ± 0.10	9	9.60 ± 0.07	1.48 ± 0.01	160 ± 7
	Ctrl (6)	181 ± 16	6.36 ± 0.03	10.19 ± 0.27	9	6.28 ± 0.01	10.61 ± 0.11	117 ± 5
	0.2	200 ± 0	10.17 ± 0.16	1.66 ± 0.13	9	10.26 ± 0.13	1.47 ± 0.01	76 ± 8
	1	235 ± 27	7.33 ± 0.02	4.12 ± 0.14	9	6.96 ± 0.62	4.35 ± 0.09	17 ± 8
	2	192 ± 0	7.17 ± 0.01	5.12 ± 0.02	9	6.37 ± 0.02	6.17 ± 0.07	11 ± 1

	4	172 ± 8	6.88 ± 0.06	8.40 ± 0.21	9	6.36 ± 0.04	8.46 ± 0.04	6 ± 1
	6	163 ± 0	6.50 ± 0.03	10.20 ± 0.02	9	6.38 ± 0.02	9.93 ± 0.05	14 ± 1
<b>Initial sulfide concentration (mM)</b>	Ctrl (2)	58 ± 5	7.00 ± 0.29	5.38 ± 0.49	18	6.11 ± 0.02	6.15 ± 0.04	28 ± 0
	Ctrl (8)	266 ± 12	7.28 ± 0.07	5.87 ± 0.11	18	6.54 ± 0.02	6.99 ± 0.11	196 ± 9
	2	59 ± 3	6.22 ± 0.56	5.25 ± 0.03	6	6.48 ± 0.01	5.85 ± 0.03	11 ± 2
	3	106 ± 9	6.99 ± 0.03	5.42 ± 0.05	6	6.51 ± 0.03	5.83 ± 0.13	14 ± 1
	5	177 ± 0	7.14 ± 0.02	5.58 ± 0.06	12	6.48 ± 0.02	6.26 ± 0.02	10 ± 1
	8	287 ± 13	7.42 ± 0.04	5.97 ± 0.09	18	6.46 ± 0.13	6.57 ± 0.23	9 ± 6
<b>Operation temperature (°C)</b>	Ctrl (4)	211 ± 83	7.35 ± 0.06	3.89 ± 0.12	9	7.22 ± 0.04	3.74 ± 0.06	177 ± 14
	Ctrl (19)	191 ± 0	7.06 ± 0.04	5.19 ± 0.09	9	6.50 ± 0.02	6.61 ± 0.07	127 ± 12
	Ctrl (31)	222 ± 0	7.47 ± 0.01	3.98 ± 0.03	9	6.71 ± 0.04	4.60 ± 0.08	130 ± 10
	4	239 ± 55	7.55 ± 0.02	3.91 ± 0.04	9	8.00 ± 0.51	3.00 ± 0.23	69 ± 10
	19	192 ± 0	7.17 ± 0.01	5.12 ± 0.02	9	6.37 ± 0.02	6.17 ± 0.07	11 ± 0
	31	212 ± 25	7.58 ± 0.02	4.00 ± 0.03	9	6.71 ± 0.03	4.37 ± 0.14	20 ± 9

### 3.2.3 Sulfide removal at simulated manure management

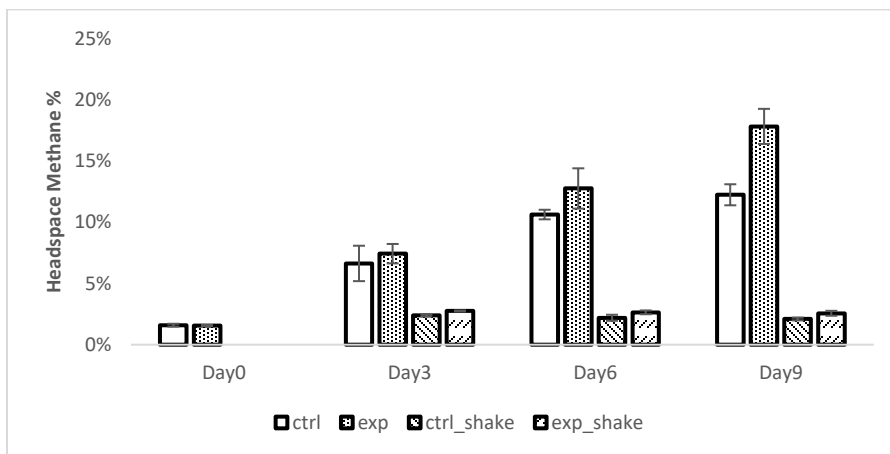
Fig. 9a showed that the sulfide removal was 95% after 9 days treatment. A transformation of manure liquid color into black during the electrochemical treatment indicated the generation of FeS. The left two columns of Fig. 9b show the corresponding H<sub>2</sub>S removal. For an initial sulfide concentration at around 5 mM, the average H<sub>2</sub>S concentration in the reactor headspace was 25,023 ppm. By applying the electrochemical treatment, a 90% removal was achieved in day 9, with a final headspace H<sub>2</sub>S concentration to be 2157 ± 855 ppm. Ni's study illustrated the H<sub>2</sub>S release mechanism that a strong H<sub>2</sub>S release can be induced due to the inside bubble breakage during the mixing [18]. The headspace H<sub>2</sub>S concentration drop after mixing found in this study indicated that the removal of sulfide in manure storage can reduce the risk of H<sub>2</sub>S release during bubble breakage due to the consequently lowered H<sub>2</sub>S concentration. On average, at the condition of applied voltage = 0.7 V, immersed electrode surface area = 19 cm<sup>2</sup>/L, initial sulfide concentration = 5 - 6 mM, and operation temperature = 19 °C, considering a zero order kinetic, the sulfide removal rate was 2.60 mg S<sup>2-</sup>/(cm<sup>2</sup>·day), R<sup>2</sup> = 0.937; considering a 1<sup>st</sup> order kinetic, the rate coefficient was 0.275 /day, R<sup>2</sup> = 0.999.



**Fig. 9** – Sulfide/Hydrogen sulfide removal in simulated experiment. (a) Sulfide removal. (Applied voltage = 0.7 V, immersed electrode surface area = 19 cm<sup>2</sup>/L, operation temperature = 19 ± 1 °C, initial sulfide concentration = 169 ± 61 mg/L, initial pH = 6.71 ± 0.11, initial conductivity = 5.36 ± 0.13 mS/cm); (b) Headspace hydrogen sulfide concentration after manually mixing (left two columns), after shaking at 210 rpm, 20 min (right two columns).

The right two columns in Fig. 9b demonstrated the part of the results from H<sub>2</sub>S shaking simulation test, in which reactors had already been sampled once with mixing involved and headspace flushed by N<sub>2</sub>. Refer to the columns of “ctrl” and “ctrl\_shake” as the conditions before and after the shaking simulation, a 75 ± 2 % recovery was calculated if no electrochemical treatment was applied. Similarly, refer to the columns of “exp” and “exp\_shake”, a 77 ± 34 % recovery was calculated if electrochemical treatment was applied. Served as the control, without applying the shaking force, the headspace H<sub>2</sub>S concentration was detected to be 5704 ± 325 ppm 20 min after N<sub>2</sub> flushing; compared to the initial concentration of 20,694 ± 1986 ppm, the H<sub>2</sub>S recovery was 28 %. Evidence was found that shaking can not only induce the bubble release, but also increase the H<sub>2</sub>S release rate from liquid phase. The H<sub>2</sub>S recovery from shaking turned out to be

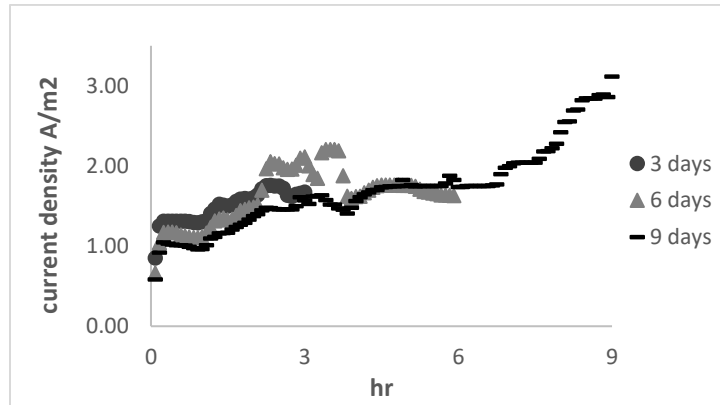
be much higher than the previous study [61], in which the H<sub>2</sub>S concentrations during 96 h 200 rpm mixing by a turbine paddle was all below 12 ppm. However, significant increases of H<sub>2</sub>S concentrations were still found if the mixing speed reached 300 rpm or higher. Supported by Ni et al. [18], the faster convection mass transport may contribute to the rapid H<sub>2</sub>S release during the manure shaking, which can be extended to the real case such as the long time manure pumping and agitation. Another evidence can be found in Fig. 10; the concentration of CH<sub>4</sub> were recorded, the average CH<sub>4</sub> recovery turned out to be 18 ± 6 %. Knowing CH<sub>4</sub> was hardly dissolved in water, the result indicated that majority portion of the H<sub>2</sub>S recovery may be contributed by the rapid mass transfer caused by the turbulence given by the shaking. As mentioned, similar H<sub>2</sub>S recoveries were found in the cases with/without electrochemical treatment; however, less risk resulted from H<sub>2</sub>S release will be caused if electrochemical treatment was applied due to the removal of sulfide, which served as the source of H<sub>2</sub>S mass transfer.



**Fig. 10** – Headspace methane concentration in percentage along the treatment period.

After 9 days, sulfate concentration from control group without electrochemical treatment dropped from 144 ± 0 mg/L to 111 ± 8 mg/L, with a 23% decrease. Sulfate concentration from experimental group with electrochemical treatment dropped from 153 ± 2 mg/L to 109 ± 8 mg/L, with a 29% decrease. The higher drop of sulfide in experimental group may result from: 1. Based on the principle of reaction rate, the removal of sulfide made the conversion into sulfide from sulfate faster by SRB. 2. Sulfate can be enmeshed in the porous iron hydroxide precipitate [62, 63]; the low power input applied may be the reason to the weak sulfate removal found in author’s study.

The current density was monitored along the comprehensive test. Shown in Fig. 11. From day 0 to day 9, current density increased over time. This may be due to the increase of manure liquid conductivity over time, from  $5.28 \pm 0.02$  mS/cm at day 0 to  $5.55 \pm 0.11$  mS/cm at day 9. Reactors sampled at day 3, 6 and 9 showed current density change overlap. Overall, the current density increased from around 1 A/m<sup>2</sup> at initial to a stable level around 1.75 A/m<sup>2</sup>, and finally reached to around 3 A/m<sup>2</sup> of the highest at day 9. An increase trend was observed.



**Fig. 11** – Current density over the treatment time.

### 3.3 Operation and management suggestion

#### 3.3.1 Improvement in produced methane concentration

Comparing the “ctrl” and “exp” results in Fig. 10, 12%, 20% and 46% higher CH<sub>4</sub> concentration was found at day 3, 6 and 9 if electrochemical treatment was applied. This finding may demonstrate two points. 1. The electrochemical treatment with experimental conditions involved in the simulation test did not inhibit the methanogenesis, supported by Lin’s study on digested dairy manure [47]. 2. Knowing that the applied voltage of 0.7 V did not produce massive H<sub>2</sub> while removing most of the sulfide (refer to 3.2.1), the increasing CH<sub>4</sub> concentration may indicate that methanogenesis can be resumed as sulfide was being removed, supported by the relevant study [64]. The higher methane production after the sulfide removal may favor the following process of manure anaerobic degradation, in which manure can generate methane at a faster rate without causing any further concerns brought by H<sub>2</sub>S, e.g. transport pipe/engine corrosion. Meanwhile, the electrochemical treatment is suggested to be applied few weeks before the manure pumping event. The first reason is that a strong H<sub>2</sub>S burst from manure storage may

only happen during the high turbulence condition during the pumping/agitation. The second reason is that the massive CH<sub>4</sub> production during the storage period after the removal of sulfide may raise concerns of trapped gas bubbles accumulation and explosion.

### 3.3.2 Headspace hydrogen sulfide concentration versus temperature

The H<sub>2</sub>S levels in the reactor headspace measured during the low carbon steel experiments were recorded in Fig. 12. The reading from 19 °C has the most readings and constitutes the main part of this graph. For other points of 4 °C and 31 °C, fewer readings were taken to support the H<sub>2</sub>S distribution profile. On the graph, H<sub>2</sub>S increases as the aqueous sulfide, therefore, by reducing the aqueous sulfide from the swine manure, the corresponded H<sub>2</sub>S level will also drop. The H<sub>2</sub>S and aqueous sulfide distribution can be understood by using Henry’s law, which suggested an equilibrium state between gaseous and aqueous phases. Hence, lowering the H<sub>2</sub>S releasing by precipitating the aqueous sulfide into FeS is feasible. Trendlines can be made to illustrate H<sub>2</sub>S activity under different temperatures. At 4°C, 1 ppm of aqueous sulfide will in equivalent to 74 ppm H<sub>2</sub>S; at 19°C, the equilibrium H<sub>2</sub>S concentration increased to 143 ppm, while at 31 °C, the coefficient increased to 408. Therefore, if considering the H<sub>2</sub>S risk in the swine barn, the highest risk will be in the summer; the warmer temperature will not only favor the growth of SRB [65], increasing the sulfide production, but also increases the potential H<sub>2</sub>S being released.

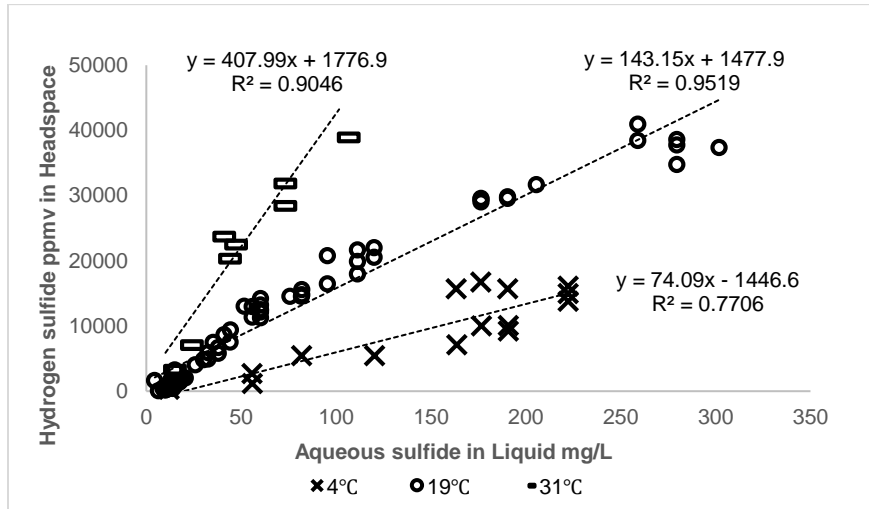


Fig. 12 – Aqueous sulfide and hydrogen sulfide equilibrium concentrations at different temperatures.

### 3.3.3 Oxidation/Reduction Potential as a sulfide concentration indicator

The ORP was recorded during the low carbon steel experiments. As shown in Fig. 13, the logarithm of sulfide concentration is negatively proportional to the ORP. For the sulfide concentration involved in this graph ranges from the highest of 134 mg/L to the lowest of 0.6 mg/L, and the corresponding ORP level ranges from the highest of -455 mV to the -174 mV. The observation of the relationship between aqueous sulfide concentration and ORP suggested an instant way to give a rough estimation of the sulfide level.

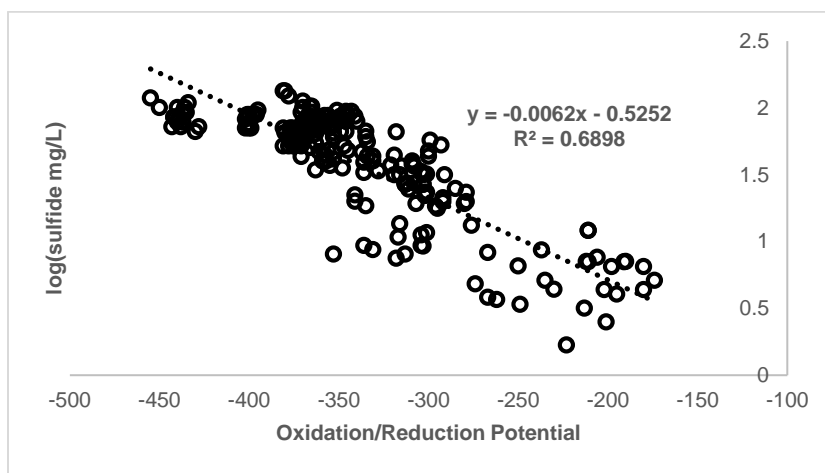


Fig. 13 – Logarithm of aqueous sulfide vs Oxidation/Reduction Potential.

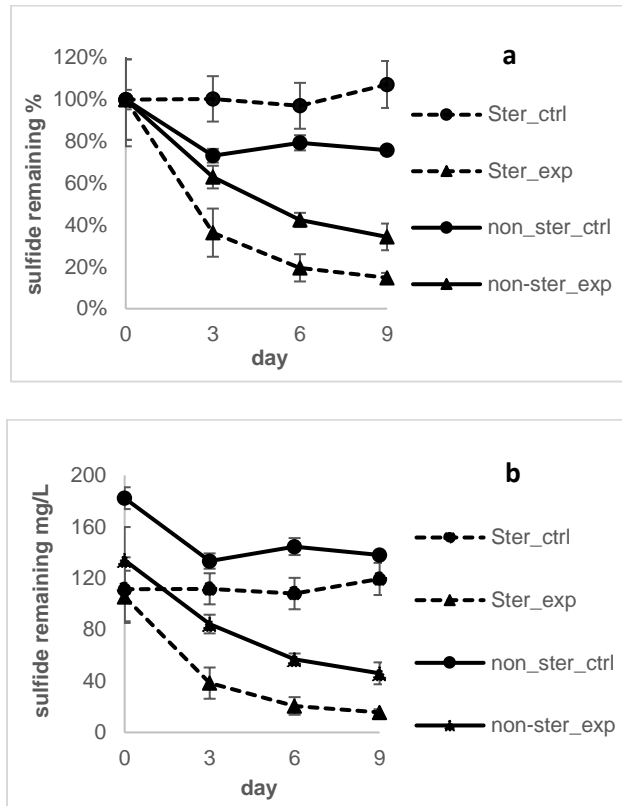
## 3.4 Extension study

### 3.4.1 Effect of sterilization and non-sterilization on swine manure

Refer to Fig. 14 and Table 6, a 9 days electrochemical treatment reduced sulfide concentration in sterilized reactors by 87% (91 mg/L), and non-sterilized group by 66% (88 mg/L). Despite a significant difference ( $p$  values  $< 0.05$ ) was detected using the percentage based regression analysis, weak evidence ( $p$  values  $> 0.05$ ) was suggested in amount based analysis. For non-sterilized reactors, higher conductivities were found, so the electrochemical sulfide removal should be more favored. It was still not clear whether a significant difference existed between the sterilized and non-sterilized groups, however, the decreasing sulfide concentration in non-



sterilized control group and the stable concentration found in sterilized control group may suggest that the activity brought by the bacteria have an impact to the sulfide in swine manure.



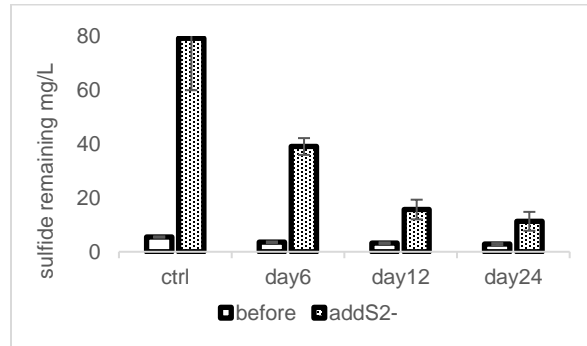
**Fig. 14** – Aqueous sulfide removal from sterilized & non-sterilized swine manure with low carbon steel as electrode. (Applied voltage = 0.7 V, immersed electrode surface area =  $19 \text{ cm}^2/\text{L}$ , operation temperature =  $19 \pm 1^\circ\text{C}$ ). (a) sulfide unit in percentage. (b) sulfide unit in mg/L.

**Table 6** – Temperature test initial and final conditions.

	initial sulfide (mg/L)	Treatment time (hr)	Initial pH	initial conductivity (ms)	final pH	Final conductivity (ms)	Sulfide Remaining (mg/L)
<b>Ster_ctrl</b>	$111 \pm 25$	9	$6.84 \pm 0.31$	$5.69 \pm 0.25$	$6.56 \pm 0.12$	$6.68 \pm 0.30$	$119 \pm 12$
<b>Nonster_ctrl</b>	$182 \pm 8$	9	$6.61 \pm 0.01$	$6.55 \pm 0.20$	$6.46 \pm 0.02$	$7.16 \pm 0.06$	$138 \pm 2$
<b>Ster_exp</b>	$105 \pm 20$	9	$6.92 \pm 0.04$	$5.38 \pm 0.26$	$6.68 \pm 0.04$	$6.45 \pm 0.07$	$14 \pm 0$
<b>Nonster_exp</b>	$134 \pm 26$	9	$6.60 \pm 0.01$	$6.63 \pm 0.07$	$6.49 \pm 0.03$	$6.49 \pm 0.11$	$46 \pm 9$

### 3.4.2 Sulfide removal potential under constant electrochemical treatment

Refer to Fig. 15, after electrochemical treatment for different days, aqueous sulfide concentrations from control, day 6, day 12 and day 24 groups were 5 mg/L, 4 mg/L, 3 mg/L and 3 mg/L, respectively. After the dosing of external sulfide at day 24, the manure sulfide concentrations increased to 79 mg/L, 39 mg/L, 16 mg/L and 11 mg/L, respectively. A longer post-treatment time indicated a stronger inhibition to sulfide removal to any follow-up sulfide being introduced. The extension of the treatment may not be suggested for any further prevention due to the recovery of methanogenesis,



**Fig. 15** – Sulfide removal potential test with low carbon steel as electrode. (Applied voltage = 0.7 V, immersed electrode surface area = 19 cm<sup>2</sup>/L, operation temperature = 19 ± 1°C; initial sulfide concentration = 4 ± 1 mg/L).

#### Chapter 4: Summary

An electrochemical method was proved to be feasible in H<sub>2</sub>S/aqueous sulfide removal from the swine manure. By removing the aqueous sulfide, the H<sub>2</sub>S level in trapped gas bubbles can be reduced as well, and eventually, much lower level of H<sub>2</sub>S would be released during the swine manure pumping event. Low carbon steel was a suitable material to be applied. Other important notes include:

1. The interference swine manure solids may bring to S<sup>2-</sup> measurement device should be noted. Significant misleading measurements can be obtained. Supernatant obtained from any liquid and solid separation method was suggested as an acceptable test solution to measure S<sup>2-</sup> concentrations.
2. A sufficiently high voltage should be applied to activate significant sulfide removal. For low carbon steel as the final selected electrode, 0.7 V was an acceptable power level to maximize the sulfide precipitation at anode and minimized the H<sub>2</sub> generation at cathode

3. The cathode hydroxide generation can help maintain the manure storage pH level. The elevation of conductivity brought by the manure thickness made electrochemical technique feasible to be applied.
4. A smaller electrode area led to a slower but lower-cost sulfide removal process. The treatment process followed a 1<sup>st</sup> order kinetic model. Zero order kinetic can also be applied for a rough estimation. Manure solid content (< 6%) and operation temperature did not significantly affect the process performance.
5. Constant liquid disturbance can greatly accelerate the H<sub>2</sub>S releasing.
6. The concentration of methane production was substantially increased during the electrochemical sulfide removal. Therefore, this technique is suggested to be applied right before the swine manure removal event due to the follow-up methane recovery. Oxidation/Reduction Potential can be used as a quick indicator along the electrochemical treatment. A cool swine manure storage temperature is suggested to reduce the H<sub>2</sub>S emission

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