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BREAKDOWN OF HYDROGEN SULFIDE IN SEAWATER UNDER DIFFERENT RATIO OF DISSOLVED OXYGEN / HYDROGEN SULFIDE

(Penguraian Hidrogen Sulfida dalam Air Laut dengan Nisbah Oksigen Terlarut / Hidrogen Sulfida yang Berbeza)

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Abstract

Breakdown of hydrogen sulfide (H_2S) in seawater is highly dependent on both the concentration of dissolved H_2S and dissolved oxygen (DO). A simple correlation was found in the H_2S dissociation and ratio of [DO/H_2S]. When the [DO/H_2S] ratio is more than one, H_2S breakdown rapidly, resulting in a short half-life of H_2S in the seawater (in a time scale of minute). When the dissolved oxygen is not a limiting factor, H_2S breakdown in a first order reaction. Nevertheless, when [DO/H_2S] ratio is less than 1, H_2S breakdown in the seawater becomes slower, resulting in a longer H_2S half-life (in a time scale up to hours). In this case, the H_2S breakdown in a pseudo-second order reaction. This pseudo-second order reaction is commonly reported by other investigators. This study also investigated the relation between the concentration of dissolved H_2S and pH changes during H_2S dissociation in the seawater. The pH is lowered with increasing concentration of initial H_2S in the seawater but appears to reach an asymptotic low value of about 4 as the dissolved H_2S approaches its saturation limit in the seawater at about 2,500 mg L^{-1}.

Keywords: hydrogen sulfide, dissolved oxygen, oxidation, seawater, H_2S dissociation

Abstrak

Penguraian hidrogen sulfida (H_2S) dalam air laut sangat bergantung kepada kepekatan kedua-dua H_2S terlarut dan oksigen terlarut (DO). Satu kolerasi mudah telah ditemui antara penguraian H_2S dan nisbah [DO/H_2S]. Apabila nisbah [DO/H_2S] melebihi satu, penguraian H_2S adalah cepat, menyebabkan separuh hayat H_2S yang pendek dalam air laut (dalam skala masa minit). Dalam keadaan yang mana oksigen terlarut bukan faktor penghad, penguraian H_2S merupakan tindak balas tertib pertama. Namun, apabila nisbah [DO/H_2S] kurang daripada satu, penguraian H_2S dalam air laut menjadi lambat, menyebabkan separuh hayat H_2S yang lebih lama (dalam skala masa jam). Dalam kes ini, penguraian H_2S adalah tindak balas pseudo tertib kedua. Tindak balas pseudo tertib kedua ini biasa dilaporkan oleh ramai penyelidik. Kajian ini turut menyiasat hubung kait antara kepekatan H_2S terlarut dan perubahan pH semasa penguraian H_2S dalam air laut. Nilai pH jadi rendah dengan peningkatan kepekatan awal H_2S dalam air laut tapi ia mencapai nilai asimptot yang rendah dalam lingkungan 4 apabila kepekatan H_2S terlarut menghampiri had ketepuannya dalam air laut pada kepekatan 2,500 mg L^{-1}.

Kata kunci: hidrogen sulfida, oksigen terlarut, pengoksidaan, air laut, penguraian H_2S

Introduction

Hydrogen Sulfide (H_2S) gas is one of the potential contaminant found in oil and gas production. H_2S is normally formed in oil and/or gas reservoirs through the decomposition of organic matter under anaerobic condition by microbes. Typically, such H_2S will be removed from the main hydrocarbon stream and disposed off to increase the sales value of the sweetened hydrocarbon. In the ocean, H_2S is mainly formed through geochemical processes during deep sea volcanic activities including hydrothermal vents [1]. When H_2S is present in the seawater in dissolved form, it dissociates into hydrosulfide (HS^-), which is the product of the first dissociation equilibrium (K_{a1}). The second dissociation equilibrium (K_{a2}) produces the sulfide ion (S^{2-}). H_2S is a weak acid, with pK_{a1} being reported by various investigators in the order of 7.0 [2-5] and pK_{a2} in the order of 12.5 [6]. Due to the first dissociation of H_2S to HS^-, the concentration of aqueous H_2S will decrease with increasing pH in water. At pH 7.0, the concentration ratio of the aqueous H_2S to HS^- is approximately 1:1. As the pH increases beyond 7.0, the ratio of the concentration of HS^- to aqueous H_2S increases. Sulfide ion (S^{2-}), which is the product of the second dissociation becomes significant, only when pH is above 12.

The hydrosulfide ion is susceptible to oxygenation reactions under aerobic condition in seawater. The oxygenation of HS^- is rather complex, involving a multitude of chemical reactions, producing various intermediate and final products, amongst others, the following possible reactions 1 – 3 [7, 8]:

$$2HS^- + 3O_2 \rightarrow 2SO_3^{2-} + 2H^+ \quad (1)$$

$$HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+ \quad (2)$$

$$2HS^- + 2O_2 \rightarrow S_2O_3^{2-} + H_2O \quad (3)$$

In the presence of relatively high concentration of dissolved oxygen (DO), the ion species of sulfite (SO_3^{2-}) is stable. Even so, some of the SO_3^{2-} species would also be oxidized to sulfates (SO_4^{2-}) [7, 9]. Hence, it is apparent that the actual overall oxidation rate of H_2S in seawater varies depending on the conditions studied. A simplified gross measure of the overall breakdown of H_2S in seawater due to various reactions shown above can be depicted by the H_2S half-life; which is a measure of the time taken to lower the H_2S concentration from its initial value to half the initial value. Various publications have provided different H_2S half-life values, depending on the reaction conditions investigated. Göte and Alexander [10] reported that the H_2S half-life of about 17 minutes at constant dissolved oxygen concentration of 5.4 mg L^{-1} and 25 °C in seawater. Sharma and Yuan [11] reported H_2S half-life of 25 minutes for treated domestic wastewater initially containing about 6 mg L^{-1} of H_2S and 8 mg L^{-1} DO, while Asaoka et al. [12] reported an *in-situ* half-life of approximately 50 minutes in the Etajima Bay, which contains about 28 mg L^{-1} of sulfide.

Decomposition of the H_2S becomes more complicated when microbial degradation is also taking place [13] or when catalytic metals are present [14]. Oxidized metals such as Fe(III), Mn(III) and Mn(IV), for example, are efficient catalysts to overcome the kinetic barrier for the chemical oxidation of sulfides [15]. The interaction of all these factors in the seawater leads to unpredictable outputs in the tropical marine environment. It is apparent that the half-life of H_2S dissociation in such waters is quite complex and dependent on the physical chemical properties as well as biological assemblage of the seawater. Thus, whenever the rate of H_2S decomposition is the intended subject, invariably there is a need to conduct *in-situ* verification using the actual seawater source. Understanding the rate of H_2S breakdown in seawater is important in environmental management as it plays an important role in toxicity and ecological footprint of the toxic gas in the marine environment. Hence, this paper describes the experiments undertaken to determine the rate of H_2S breakdown in seawater obtained from the Terengganu offshore, as representative of the offshore water of Peninsular Malaysia. The study includes analysis to derive appropriate rate equations and rate constant(s) for the H_2S breakdown in seawater as well as estimations of the dissociation half-life. In addition, the effect of H_2S dissociation on the pH of the resultant solution is of particular interest. In freshwater, the dissolution of H_2S into HS^- ions generate protons, which effectively lowers the pH of the solution. However, in seawater, the natural alkalinity of the seawater tends to counteract the lowering of the pH through various carbonaceous compounds in the seawater carbonate equilibrium. This can result in a complex, non-linear pH correlation with concentration of H_2S dissolution. In this study, it is desired to establish an empirical relationship between the effect of H_2S dissolution and resultant pH of the seawater solution.

Materials and Methods

Materials

Seawater used in this experiment was collected from the South China Sea off Terengganu. The seawater was then filtered and acclimatized for one week before use. 1 L Kipps apparatus was used to produce the hydrogen sulfide (H_2S) gas used in this study. In the Kipps apparatus, excess pyrite (Fe_2S) was allowed to react with hydrochloric acid (20%) to generate H_2S gas. The gas was bubbled into 1 L oxygen-free deionized water for 24 hours to produce an approximately 2000 mg L^{-1} H_2S aliquot for the subsequent experiments. Oxygen free water was prepared by purging deionized water with pure nitrogen at 30 mL s^{-1} for 40 minutes. High Purity oxygen and nitrogen (> 99 %) gases were used in this study. All the chemicals used in the study were of analytical grade and supplied by Merck Co.

Determination of hydrogen sulfide in seawater

Hydrogen sulfide (H_2S) probe (MS-AQUA) was used to monitor H_2S concentration in the experiments. Analysentechnik GmbH develops the amperometric MS-AQUA H_2S micro sensor for *in-situ* determination of dissolved H_2S or Total sulfide in aqueous solution within a pH range of 0 to 8. Other than the ion sensitive electrode (ISE), the MS-AQUA is the only method for *in-situ* [H_2S/ Total Sulfide] measurement. MS-AQUA is more relevant as compared to the other ISEs because the workable pH range of MS-AQUA is more relevant to the study undertaken. The accuracy and the concentration of the MS-AQUA below 3 mg L^{-1} is essentially better than the other ISEs. Table 1 shows the technical data extracted from the technical manual of the sensor. The H_2S probe was pre-calibrated by the manufacturer and was validated with standard solutions by comparing the concentration obtained from the probe and the standard methods (APHA 4500-S^{2-}F., Iodometric method and APHA 4500-S^{2-}H, calculation of unionized H_2S) [16]. Dissolved oxygen and pH were determined by using YSI 550a and the pH probe of the MS-AQUA respectively.

Table 1. Technical specification of MS-AQUA H_2S probes used in the study

Technical Specification	**Range**
Measurement range	
• Type I*	• 10 µg L^{-1} – 3 mg L^{-1} H_2S
• Type II	• 50 µg L^{-1} – 10 mg L^{-1} H_2S
• Type III*	• 500 µg L^{-1} – 50 mg L^{-1} H_2S
Accuracy of the sensor	2 %
Temperature range	0°C – 30°C
pH range	0 – 8
Salinity range	< 40 ppt (g L^{-1})
Signal Interference	
• Carbon dioxide	Up to 25.38%
• Methane	Up to 5.78%
• Hydrogen	Up to 0.544%
• Ammonia	Up to 1000 ppm
• Carbon monoxide	Up to 92 ppm
• Carbon disulfide	Up to 5%
• Acetic acid	Up to 1 mol L^{-1}
• Dimethyl sulfide	Up to 10%
• Ethanol	Up to 10%

* Sensors used in this study

APHA Method 4500–S^2-F [16] was also used to validate the reading from the probe as well as to determine those concentration that fell beyond the measurement range of the MS-AQUA. In the case where the H_2S level exceeded the measurement range, water sample was collected from the experimental chamber by using syringe acted as a piston to drive water sample out of the vessel. Samples drawn out from the experiment was analyzed for its pH and H_2S level right after sampling. Briefly, 20 mL of iodine solution (0.025 N) followed by 2 mL 6N HCl was poured into a 500 mL flask. An amount 200 mL sample was discharged under the solution surface into the flask. More iodine solution was added if the color of the iodine disappeared. The sample was then back-titrated with standard sodium thiosulfate solution (0.025 N). A few drops of starch solution were added as indicator for the end point (disappearance of blue color). The concentration of total sulfide was then calculated, taking into account the dilution factor during titration. The concentration of unionized H_2S is then calculated by multiplying the dissociation factor at the measured pH with the total sulfides as stipulated in APHA Method 4500–S^2-H [16].

Breakdown of hydrogen sulfide in seawater

Experimental chamber as shown in Figure 1 was used in this study. The chamber consists four major components; 1. H_2S, temperature and pH probes, 2. Aliquot injection port, 3. Dissolved oxygen probes, and 4. Magnetic bar and stirrer. The experimental chamber was incubated in a 20 L water bath. The reactor vessel was first filled with 2 L of seawater. Pure oxygen and nitrogen from gas cylinders were used to adjust the level of dissolved oxygen in the seawater. 50 mL syringe was used to inject concentrated H_2S aliquot through the injection port into the reactor. The volume of concentrated H_2S solution injected into the reactor was obtained based on dilution equation ($M_1V_1 = M_2V_2$) to make up the desired H_2S concentration. The volume of injection was limited to less than 2% of the total reactor volume. No head space was permitted in the chamber throughout the experiment. In order to avoid leakages, all ports were sealed with silicon glue. Magnetic bar and stirrer (300 rpm) were used to homogenize the aliquot and seawater in the experimental vessel. The experiments were conducted in the laboratory at 28°C, pH 8.0 and 30 ppt. Experiment started one minute after injection of the H_2S aliquot. This is to ensure sample homogeneity in the vessel. Readings were recorded continuously by using a camcorder and then manually transferred into excel spreadsheet. The data were then used to determine the reaction order, rate and constant. All the experiments were conducted in triplicate.

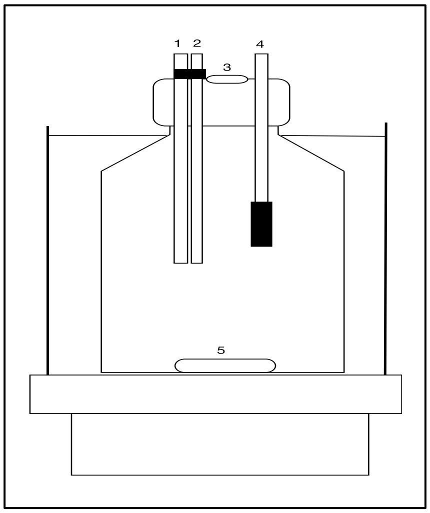


Figure 1. Experimental setup for investigation of H_2S removal in seawater. 1. H_2S, temperature and pH probes, 2. Aliquot injection port, 3. Dissolved oxygen probe, 4. Magnetic bar and stirrer

H_2S solubility and pH changes in seawater

Prior to the main H_2S breakdown rate experiments, solubility of the H_2S in seawater was tested using the experimental setup as shown in Figure 2. In the experiment, H_2S gas generated from Kipps apparatus was bubbled through the seawater at 28°C, 30 ppt and pH 8.0 in a 2 L vessel through port 2. Port 4 is the vent for excess gas. During sample withdrawal, port 4 was clipped and the syringe (5) was used as a piston to drive water sample out of the vessel through port 3. The concentration of the H_2S, temperature, pH and dissolved oxygen were determined immediately. The experiments were conducted in a 20 L water bath for consistent temperature at 28 °C (±0.5 °C). All the experiments were conducted in three replicates.

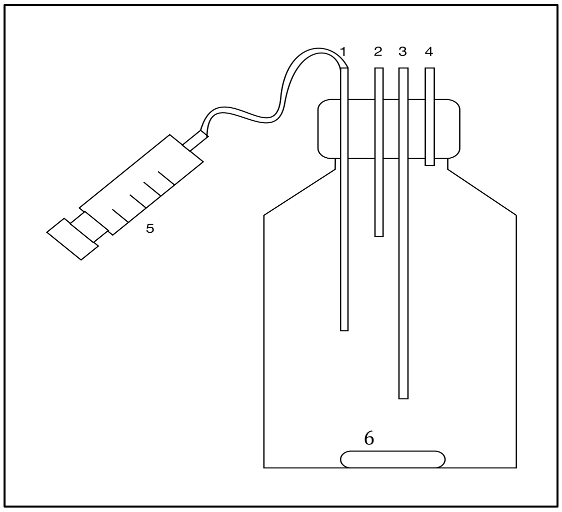


Figure 2. Experimental setup for investigating hydrogen sulfide solubility. 1. Piston inlet for sampling, 2. Gas inlet from Kipps apparatus, 3. Sample outlet, 4. Excess gas exhaust, 5. Syringe, 6. Magnetic bar

Determination of reaction order, rate constant and half-life

Data obtained from H_2S breakdown experiments were used to determine the reaction order, rate constant and half-life of the H_2S removal. Reaction kinetics were studied based on computation procedure of Han et al. [17]. The reaction orders, rate constants and half-life were obtained by using graphical method. In the case where the dissolved oxygen is in excess, the reaction constant and the breakdown rate of the H_2S would resemble the pseudo-first order (K_1) reaction as (4):

$$\frac{d[H_2S]}{dt} = -K_1[H_2S]_t \tag{4}$$

Where, $[H_2S]_t$ is define as concentration of hydrogen sulfide at time t and K_1 is define as rate constant.

While, the reaction constant and the breakdown rate of the H_2S resemble a second order reaction, it represented as (5):

$$\frac{d[H_2S]}{dt} = -K_2[H_2S]_t[O_2]_t \tag{5}$$

where, $[H_2S]_t$ is define as concentration of hydrogen sulfide at time t, $[O_2]_t$ is define as concentration of dissolved oxygen at time t and K_2 is rate constant.

The reaction constant for second order reaction, K_2, can be assessed by dividing K_1 with $[O_2]_t$. K_1 can also be derived from the concentration graphs by computing the gradient of the H_2S concentration over the linear portion of the decline and dividing by the average concentration of H_2S over the considered range. Comparing equations (4) and (5), K_2 can be estimated from $K_1/[O_2]$. Since the DO concentration in the seawater for the case of lower DO/ H_2S concentration ratio is expected to decline in tandem with the breakdown of H_2S, estimation of K_2 in this case, is applicable only over a narrow time range where the DO concentration within that time range does not resulted in a significant differences in K_2 and K_1. In this study, such approximations are restricted to the first few minutes of the experiments, where the H_2S concentration decline is still linear and the DO has not declined more than 50% of its initial concentration. Integrating equation (5) provides a mathematical estimate of the H_2S dissociation half-life for the experiments (equation 6 - 8):

$$\int \frac{\mathrm{d[H2S]}}{\mathrm{[H2S]}}\mathrm{dt} \;\; =-1\int K_2\,[O_2]$$

$$\frac{1}{[O_2]_o-[H_2S]_o}\ln\frac{[O_2]_t[H_2S]_o}{[O_2]_o[H_2S]_t}=K_2t \tag{6}$$

When $[O_2]_o$ is much higher than $[H_2S]_o$, $[O_2]_o \sim [O_2]_t$, equation (6) become (7)

$$\frac{1}{[O_2]_t}\ln\frac{[H_2S]_o}{[H_2S]_t}=K_2t$$

$$[H_2S]_t=[H_2S]_o e^{-[O_2]_t K_2 t} \tag{7}$$

Half-life can be determined based on equation (7), as $[H_2S]_t = 0.5[H_2S]_o$, thus

$$t_{1/2}=\frac{ln0.5}{-K_2[O_2]_o} \tag{8}$$

Statistical analysis

Paired t-test was performed to compare if there is significant different in the reading obtained from H_2S probe (MS-AQUA) and the standard methods [16]. The statistical analysis was performed by using open source software, R statistics version 3.3.2.

Results and Discussion

Validation of H_2S probe

Data obtained by using the H_2S probe (MS-AQUA) was cross checked with APHA 4500-S^{2-}F standard method. Experiments and analysis on different concentration of H_2S standard solution was conducted to validate the corresponding measurement on the sensor. Results obtained from the probe were not significantly different (paired t-test, $p>0.05$) from those obtained by using APHA standard method and there is a correlation between the data values. (Pearson, $P < 0.05$, $R^2 = 0.9974$). Figure 3 shows the correlation of H_2S concentration obtained by using probe and the standard method. Validation of the H_2S probe is important because the probe is considered new in the market and there are only few reports on its efficiency in measurement. The probe is responsive towards H_2S even it exceeded the measurement range recommended by the manufacturer although the last two points in the validation curve (Figure 3) starts showing deviation from the proportionality.

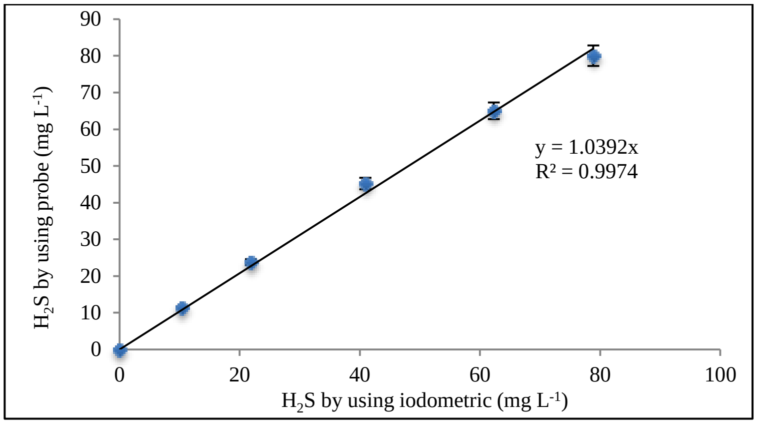


Figure 3. H_2S Probe (MS-AQUA) measurement correlated with concentration determined by using APHA standard methods (4500-S^{2-}F and APHA 4500-S^{2-}H)

H_2S solubility and pH changes in seawater

When H_2S was continuously bubbled into the seawater, the seawater pH dropped from an initial value of pH 8.01 down to pH 4.27 as the H_2S concentration was approaching 2312 mg L^{-1} (Figure 4). At 28 °C, the concentration of H_2S was saturated at about 2500 mg L^{-1} in 30 ppt seawater in the experiments. It is anticipated that H_2S would equilibrate and evolve into the vapor space at the saturation state. Hence, the H_2S concentration used in this study was limited to 1500 mg L^{-1} to reduce experimental errors and in terms of safety consideration.

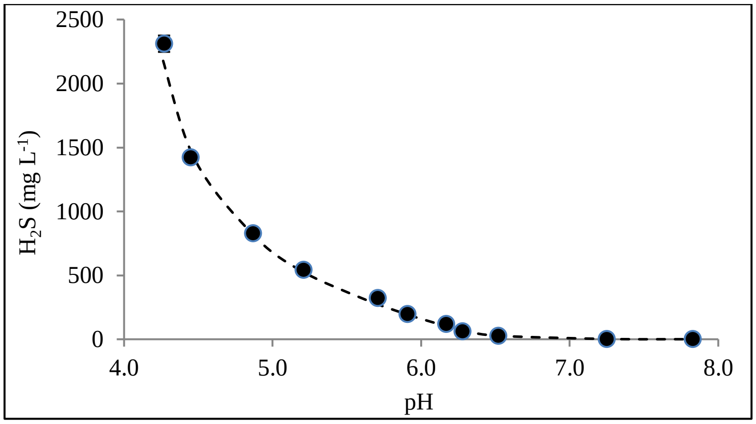
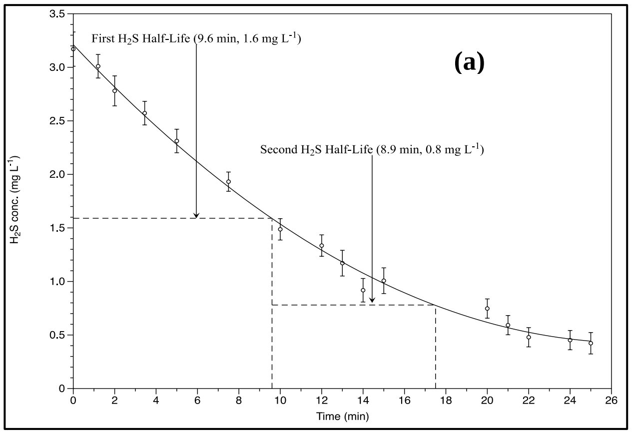


Figure 4. Effect of hydrogen sulfide concentration on seawater pH

Hydrogen sulfide breakdown in seawater at different [DO]/[H_2S] ratio

In the presence of excess dissolved oxygen in seawater, dissolved hydrogen sulfide (H_2S) is oxidized rapidly in the seawater. Figure 5 shows the H_2S breakdown against time in seawater under aerobic condition. At an initial dissolved oxygen of 10.2 mg O_2 L^{-1} (Figure 5a), the H_2S decomposed from initial 3.2 mg L^{-1} into half of its initial concentration at 1.6 mg L^{-1} in about 10 minutes when the ratio of [DO/H_2S] is 3.4 (Figure 5a). The H_2S concentration was further decomposed in the seawater. The subsequent half-life of the H_2S concentration 1.6 to 0.79 mg L^{-1} was about 9 minute. We repeated the experiment by introduced an initial concentration of 5.2 mgL^{-1} H_2S under a [DO/H_2S] ratio of 3.2 (Figure 5b) at an initial dissolved oxygen of 17.4 mg O_2 L^{-1}, after 10.6 minutes, the H_2S concentration dropped to half of its initial concentration. The H_2S concentration in this experiment further decomposed to 1.3 mgL^{-1} after 10.4 minutes. In both experiments, the dissolved oxygen remained above 4 mgL^{-1} at the end of the experiments. On average, H_2S breakdown at 9.9 ± 0.8 minute in the seawater when dissolved oxygen is in excess. The H_2S breakdown reaction appears to be a first order reaction, when the dissolved oxygen is not a limiting factor.



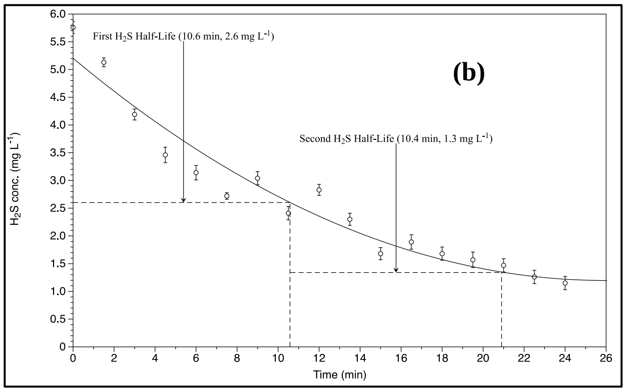


Figure 5. Hydrogen sulfide breakdown in the seawater at (a) initial dissolved oxygen of 10.2 mg L^{-1}, [DO/H_2S] ratio 3.4 (b) initial dissolved oxygen of 17.4 mg L^{-1}, [DO/H_2S] ratio 3.2

Hydrogen sulfide breakdown in seawater at low [DO/H_2S] molarity ratio

Under low [DO/H_2S] molarity ratio, as the hydrogen sulfide (H_2S) is oxidized, the concentration of DO in the seawater decreased in tandem with the decrease in H_2S concentration. In this case, H_2S breakdown no longer resemble a first order reaction due to the dissolved oxygen depletion in the seawater. The H_2S breakdown is rather regulated by the availability of the dissolved oxygen. Figure 6 shows a typical H_2S concentration decline as it is reacted with DO under a low [DO/H_2S] concentration ratio. The H_2S half-life at initial conditions of the experiment was estimated based on equation (4) provided earlier. Further experiments were conducted at low [DO/H_2S] ratios to derive the correlations of H_2S breakdown in seawater and determine the approximate H_2S half-life under those conditions. The experiments were conducted such that the [DO/H_2S] molarity ratio range spanned from less than 0.1 to above 10. This would provide adequate evidence of any correlation between the concentration ratio and the dissociation half-life. Table 3 below provides the measured H_2S half-life for various [DO/H_2S] ratio.

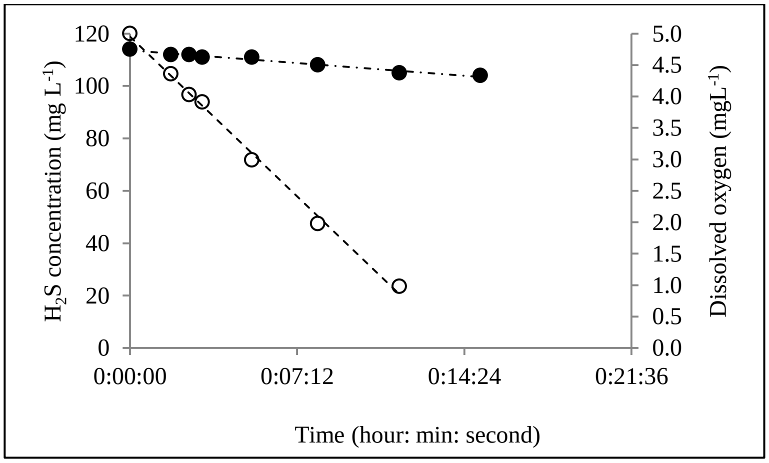


Figure 6. Typical hydrogen sulfide breakdown in seawater at low [DO/H_2S] concentration ratio [H_2S initial concentration = 114 mg L^{-1}; DO initial concentration = 5 mg L^{-1}]. Open blank circle indicates dissolved oxygen while filled circle indicates concentration of hydrogen sulfide in seawater

Table 3. H_2S Half-life at various [DO/H_2S] ratio

[DO/H_2S] Ratio	**H_2S Initial Conc. (mg L^{-1})**	**DO Initial Conc. (mg L^{-1})**	**H_2S Half-life (min)**
0.05	114.0	5.0	82.1
0.16	92.7	14.0	35.7
0.49	43.2	20.0	17.3
3.41	3.2	10.2	10.3
12.02	1.5	16.4	3.3

As can be seen from Table 3 and Figure 7, the H_2S half-life versus [DO/H_2S] concentration ratio reveal a non-linear regression. The log transformed half-life and [DO/H_2S] ratio showed a significant regression ($P < 0.05$, $y = -0.54x + 1.16$, $R^2 = 0.9687$). Figure 7 shows the H_2S half-life plotted against the molarity ratio of [DO/H_2S] in a log-log plot. The relationship between the [DO/H_2S] versus H_2S half-life resembles an inverse relationship, where decomposition of H_2S is very much dependent on the presence of dissolved oxygen in the seawater. Based on Figure 7, when [DO/H_2S] concentration ratio is lower than 0.07, the H_2S half-life will extend beyond hour. When the [DO/H_2S] ratio is higher than 1.1, the H_2S half-life will fall within 10 minutes.

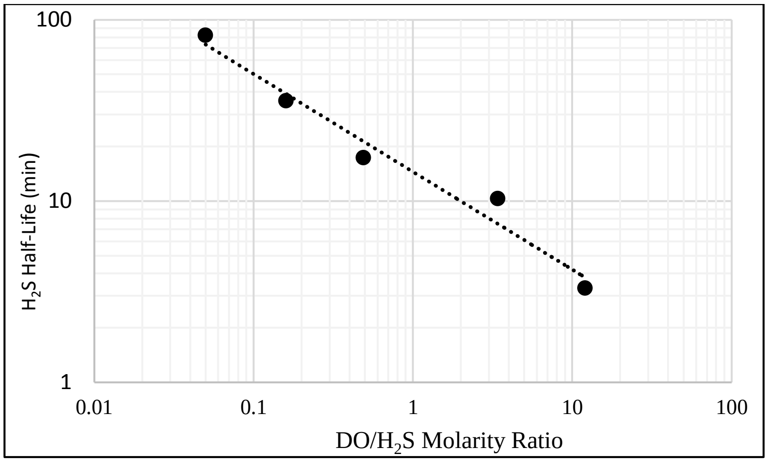


Figure 7. Hydrogen sulfide half-life versus the molarity ratio of [DO/H_2S] in a log-log plot

Table 4 shows a compilation of H_2S half-life reported in various reports. The H_2S half-life reported ranged from 17 minutes up to 55 days. Our current finding is consistent with the previous reports which reported that oxidation of H_2S resembles a first order reaction in seawater when the dissolved oxygen is high and unlimited and becomes a second order reaction when dissolved oxygen is depleting [7, 8]. Nevertheless, both group of researchers reported that oxidation of H_2S in seawater involved a series of complicated processes that are dependent on the composition and conditions of seawater. Different seawater conditions; which include physical, chemical and biological parameters is interacting and will influent H_2S breakdown in the seawater.

Pos et al. [18] reported H_2S in seawater subjects to photo-oxidation that had a half-life of 45 ± 15 minutes in Biscayne Bay water and 147 ± 15 minutes in the Gulf stream while Heitmann and Blodau [19] reported oxidation and incorporation of H_2S by dissolved organic matter in seawater. Luther et al. [20] reported a complicated inorganic and biological mediated processes in the fate of H_2S in the seawater environment. To the best of our survey, we have not encounter any comprehensive report that reveals the total interaction of physical, chemical and biological factors into the H_2S breakdown in seawater and the complicated interaction is probably the reasons that lead to various H_2S half-life reported in the seawater.

Table 4. H_2S breakdown half-life reported in seawater

Medium	Experimental Conditions	Half-Life	References
Seawater	Temperature = 28 °C Salinity = 30 ppt Hydrogen sulfide = 1.5 – 114 mg L^{-1} DO = 5 – 16.4 mg L^{-1}	3.3 – 82.1 min	Present study
Seawater	Temperature = 9.8 °C Salinity = 30.27 ppt Total sulfide = 2.0 mg L^{-1} DO = DO: Total sulfide ratio from 8 - 2 pH = 9.6	6-28 h	[7]
Seawater	Temperature = 25 °C Salinity = 35 ppt H_2S = 0.85 mg L^{-1} pH = 8.0	26 h	[8]
Seawater	Temperature = 25 °C Salinity = Not reported H_2S = Not reported DO = 3.8 ml/l pH = Not reported	17 min	[10]
Seawater	Temperature = Not reported Salinity = 30 ppt H_2S = 20 mg L^{-1} DO = Not reported pH = Not reported	45 min	[11]
NaCl solution	Temperature = 25 °C Salinity = Not reported H_2S = Not specified DO = Saturation pH = 12	55 day	[20]
Artificial seawater	Temperature = Not reported Salinity = 16.5 ppt H_2S = 25 mg L^{-1} DO = Not reported pH = Not reported	57 min	[21]
Seawater	Not reported	2 – 5 h	[22]
Seawater	Temperature = Not reported Salinity = Not reported H_2S = 513 µg L^{-1} DO = Not reported pH = 9.6	30 min	[23]

Conclusion

Hydrogen sulfide (H_2S) breakdown in seawater is highly dependent on the concentration of dissolved H_2S and the concentration of dissolved oxygen (DO). The rate of H_2S breakdown can be generally estimated based on the molarity ratio of [DO/H_2S]. At high [DO/H_2S] ratio (> 1), the H_2S breakdown rate can be rapid, resulting in short half-life of H_2S dissociation (within 10 minutes). Under this circumstance where the dissolved oxygen is not a limiting factor in the H_2S oxidation, the breakdown rate appears as a first order reaction. However, when the ratio of [DO/H_2S] ratio is lower than 0.07, the breakdown rate became slower, resulting in longer half-life of H_2S breakdown (more than an hour's). In this case, the breakdown rate displays a second order reaction form, which concurred with reports from other investigators. This study also investigated relation between the dissolved H_2S content and pH changes in the seawater. The pH of seawater became lowered with increasing initial H_2S concentration in the seawater. It reached an asymptotic low value of about 4 as the dissolved H_2S content approaches its saturation limit in the seawater at about 2,500 mg L^{-1}.

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