The Impact of Surficial Biochar Treatment on Acute H$_2$S Emissions during Swine Manure Agitation before Pump-Out: Proof-of-the-Concept

Baitong Chen 1, Jacek A. Koziel 1,*, Andrzej Białowiec 1,2,*, Myeongseong Lee 1,3,*, Hantian Ma 4, Peiyang Li 1,*, Zhanibek Meiirkhanuly 1 and Robert C. Brown 5

1 Department of Agricultural and Biosystems Engineering, Iowa State University, Ames, IA 50010, USA; baitongc@iastate.edu (B.C.); andrzej.bialowiec@upwr.edu.pl (A.B.); leefame@iastate.edu (M.L.); peiyangl@iastate.edu (P.L.); zhanibek@iastate.edu (Z.M.)
2 Faculty of Life Sciences and Technology, Wrocław University of Environmental and Life Sciences, 37a Chelomskiego Str., 51-630 Wrocław, Poland
3 Department of Animal Biosystems Sciences, Chungnam National University, Daejeon 34134, Korea
4 Department of Civil, Construction and Environmental Engineering, Iowa State University, Ames, IA 50010, USA; hantian@iastate.edu
5 Bioeconomy Institute and Department of Mechanical Engineering, Iowa State University, Ames, IA 50011, USA; rcbrown3@iastate.edu

* Correspondence: koziel@iastate.edu; Tel.: +1-515-294-4206

Received: 11 July 2020; Accepted: 12 August 2020; Published: 16 August 2020

Abstract: Acute releases of hydrogen sulfide (H$_2$S) are of serious concern in agriculture, especially when farmers agitate manure to empty storage pits before land application. Agitation can cause the release of dangerously high H$_2$S concentrations, resulting in human and animal fatalities. To date, there is no proven technology to mitigate these short-term releases of toxic gas from manure. In our previous research, we have shown that biochar, a highly porous carbonaceous material, can float on manure and mitigate gaseous emissions over extended periods (days–weeks). In this research, we aim to test the hypothesis that biochar can mitigate H$_2$S emissions over short periods (minutes–hours) during and shortly after manure agitation. The objective was to conduct proof-of-the-concept experiments simulating the treatment of agitated manure. Two biochars, highly alkaline and porous (HAP, pH 9.2) made from corn stover and red oak (RO, pH 7.5), were tested. Three scenarios (setups): Control (no biochar), 6 mm, and 12 mm thick layers of biochar were surficially-applied to the manure. Each setup experienced 3 min of manure agitation. Real-time concentrations of H$_2$S were measured immediately before, during, and after agitation until the concentration returned to the initial state. The results were compared with those of the Control using the following three metrics: (1) the maximum (peak) flux, (2) total emission from the start of agitation until the concentration stabilized, and (3) the total emission during the 3 min of agitation. The Gompertz’s model for determination of the cumulative H$_2$S emission kinetics was developed. Here, 12 mm HAP biochar treatment reduced the peak (1) by 42.5% ($p = 0.125$), reduced overall total emission (2) by 17.9% ($p = 0.290$), and significantly reduced the total emission during 3 min agitation (3) by 70.4%. Further, 6 mm HAP treatment reduced the peak (1) by 60.6%, and significantly reduced overall (2) and 3 min agitation’s (3) total emission by 64.4% and 66.6%, respectively. Moreover, 12 mm RO biochar treatment reduced the peak (1) by 23.6%, and significantly reduced overall (2) and 3 min total (3) emission by 39.3% and 62.4%, respectively. Finally, 6 mm RO treatment significantly reduced the peak (1) by 63%, overall total emission (2) by 84.7%, and total emission during 3 min agitation (3) by 67.4%. Biochar treatments have the potential to reduce the risk of inhalation exposure to H$_2$S. Both 6 and 12 mm biochar treatments reduced the peak H$_2$S concentrations below the General Industrial Peak Limit (OSHA PEL, 50 ppm). The 6 mm biochar treatments reduced the H$_2$S concentrations below the General Industry Ceiling Limit (OSHA PEL, 20 ppm). Research scaling up to larger manure volumes and longer agitation is warranted.
Keywords: hydrogen sulfide; biocoal; livestock manure; agricultural safety; fertilizer; waste management; air pollution; odor; kinetics; Gompertz model

1. Introduction

Hydrogen sulfide (H₂S) is a serious safety concern in agriculture and other industries. Inhalation of H₂S can be harmful to both humans and livestock, and sometimes deadly. The Occupational Safety and Health Administration (OSHA) recommends the permissible exposure limits (PELs) concentration for H₂S at 20 ppm and an acceptable maximum peak above the acceptable ceiling concentration at 50 ppm, with a maximum duration of 10 min [1].

The mid-western United States has a significant presence of pork production. Many large swine buildings use deep-pits to store manure under the slatted floor for up to 1 year. When a pit is full, farmers pump-out most of the manure to fertilize their fields in the fall. Agitating manure prior to pump-out is required to incorporate sediments and efficiently empty the pits. This routine seasonal operation generates a high risk of inhalation exposure to gases released from manure. Agitating the manure can break the entrapped gas bubbles, which causes an instantaneous increase in H₂S concentration (Figure 1) [2]. Fatal accidents have been recorded involving a high concentration of H₂S owing to the agitation of manure in the past several years [3–6].

Figure 1. Schematic of the agitation process before seasonal manure pump-out from deep-pit storage under swine barn with a slatted floor. Fatal accidents are known to occur to people and livestock owing to the dangerous acute release of entrapped gases (e.g., H₂S) from stored manure during agitation.

To date, there is no proven technology to mitigate these short-term releases of toxic gas from manure. Commercial pit manure additives of the microbial mode of operation are used by some swine farmers to control gaseous emissions. Still, science-based guides, as well as more data, are needed to evaluate manure additive effect on the mitigation of gases emitted from storage [7]. Recent research on manure additives such as soybean peroxidase, zeolite, and biochar show the effectiveness of mitigating H₂S, NH₃, volatile organic compounds (VOCs), and greenhouse gas (GHG) emissions from swine manure over extended periods of time [8–13]. Additionally, we evaluated the performance of numerous commercial manure additives, but there was no overall statistically significant mitigation for gaseous emissions [14, 15].

In our previous research, we have shown that 6 mm and 12 mm thick layer treatment of biochar, a highly porous carbonaceous material, can float on manure and mitigate gaseous emissions over
extended periods (days–weeks). The mitigation effects on H$_2$S were typically the greatest on the first day of application and decreased over the duration of the trial [16]. This observation led us to explore the possibility of using surficial biochar treatment for short-term mitigation of H$_2$S emissions from swine manure. In this research, we aim to test the hypothesis that biochar can mitigate H$_2$S emissions over short periods (minutes–hours) during and shortly after manure agitation. The biochars tested had similar properties to those used for testing the spatial and temporal effects on pH near the liquid–gas interface owing to biochar addition to water [17] and manure surface [18].

Biochar has received considerable interest in the recent decade. It was proposed to be used as a soil amendment, an alternative source of fuel, and an adsorbent [19–21]. Biochar can be made from abundant biomass and waste through pyrolysis or torrefaction with no oxygen or a low-oxygen level [20–25]. Biochar’s physicochemical properties vary as a result of differences in feedstock and its pretreatment, temperature, and time of the process [20–25]. The desired properties (e.g., pH, porosity, chemical moiety) could be explored to achieve environmental sustainability goals.

The first research question was, what biochar dose should be applied? The second research question was, how could a farm-scale system (Figure 1) be scaled down for a proof-of-the-concept experiment? The third research question was, how will the agitation of manure with added biochar influence the H$_2$S emission rates? Finally, will the mitigation effect be sufficient to meet the OSHA PELs recommendations, and will the results warrant scale-up research? We hypothesized that a greater biochar dose (thickness of the surficial layer applied to manure) would increase the H$_2$S mitigation effect; proof-of-the-concept experiments could use a shorter agitation time and a smaller amount of manure; and the mitigation effect would be significant and practical enough to warrant further scale-up research.

2. Results

2.1. Gaseous Emissions Post Biochar Application and Pre-Agitation (Stage 1)

Immediately after applying RO biochar, both scenarios showed a significant reduction in emissions. The 12 mm biochar treatment reduced the concentration of H$_2$S by 68.3%, and the 6 mm biochar treatment reduced 65.1% of H$_2$S (Table 1).

| RO Biochar | Condition | Control | 12 mm Biochar | 6 mm Biochar |
|------------|-----------|---------|---------------|--------------|
| Pre-agitation H$_2$S (mg m$^{-2}$ s$^{-1}$) | 0.00181 ± 0.000503 | 0.000782 ± 0.000388 | 0.000632 ± 0.000154 |

Once the HAP biochar was applied, the 12 mm biochar treatment immediately reduced the concentration of H$_2$S by about 99%, and the 6 mm biochar treatment reduced emissions by nearly 100% for H$_2$S (Table 2).

| HAP Biochar | Condition | Control | 12 mm Biochar | 6 mm Biochar |
|-------------|-----------|---------|---------------|--------------|
| Pre-agitation H$_2$S (mg m$^{-2}$ s$^{-1}$) | 0.0146 ± 0.0206 | 0.00014 ± 0.00011 | 0 * |

* below detection limits.
2.2. Effect of the Dose on the Apparent Biochar Behavior Post-Agitation

After the agitation process, most of the biochar was still floating on the top of the manure. Some of the biochar was wetted and mixed with manure (as circled in Figure 2). The treatments with 12 mm biochar dose were visibly wetter and mixed more readily with manure than those treated with 6 mm biochar. Patches of open (not covered) manure were more prevalent to higher biochar dose. We observed similar dose-dependent behavior with surficially applied soybean peroxidase treatment to swine manure [11].

![Figure 2](image_url)

**Figure 2.** Swine manure surface: Control (left), highly alkaline and porous (HAP) biochar evenly spread on top of the swine manure (center left), 6 mm thick HAP biochar layer after agitation (center right), and 12 mm thick HAP biochar layer after agitation (right). Patches of open (uncovered) manure (red circles) were more apparent when higher biochar dose was used.

2.3. Gaseous Emissions during Agitation (Stage 2)

Both the 6 mm and 12 mm RO biochar treatment significantly \( p < 0.0001 \) reduced the total emission of \( \text{H}_2\text{S} \) by 67.4% and 62.4%, respectively (Table 3, Figure A1). The 6 mm and 12 mm RO biochar treatment resulted in a 63.0% \( (p = 0.0511) \) and 23.6% \( (p = 0.145) \) reduction in the maximum peak flux of \( \text{H}_2\text{S} \), respectively (Table 3).

**Table 3.** RO biochar treatment: the maximum peak flux and total \( \text{H}_2\text{S} \) emission during 3 min agitation (bold font signifies statistical significance).

| RO Biochar during the 3 min of Agitation | Control | 12 mm Biochar | 6 mm Biochar |
|-----------------------------------------|---------|---------------|--------------|
| Maximum peak flux while agitating, \((\text{mg} \cdot \text{m}^{-2} \cdot \text{s}^{-1})\) | 0.0504 ± 0.00078 | 0.0385 ± 0.0138 | 0.0186 ± 0.00977 |
| % Reduction of maximum peak flux while agitating | – | 23.6 \( (p = 0.145) \) | 63.0 \( (p = 0.0511) \) |
| Total emission during 3 min agitation, \((\text{mg} \cdot \text{m}^{-2})\) | 7.18 ± 0.644 | 2.7 ± 0.698 | 2.34 ± 0.472 |
| % Reduction of total emissions during 3 min agitation | – | **62.4** \( (p < 0.0001) \) | **67.4** \( (p < 0.0001) \) |

Both the 6 mm and 12 mm HAP biochar treatment significantly \( p < 0.0001 \) reduced the total emission of \( \text{H}_2\text{S} \) by 66.6% and 70.4%, respectively (Table 3, Figure A2). The 6 mm and 12 mm RO biochar treatment resulted in 60.6% \( (p = 0.05804) \) and 42.5% \( (p = 0.1249) \) reduction in the maximum peak flux of \( \text{H}_2\text{S} \), respectively (Table 4).
Table 4. HAP biochar treatment: the maximum peak flux and total H₂S emission during 3 min agitation (bold font signifies statistical significance).

| HAP Biochar during the 3 min of Agitation | Control | 12 mm Biochar | 6 mm Biochar |
|------------------------------------------|---------|---------------|--------------|
| Maximum peak flux while agitating, (mg·m⁻²·s⁻¹) | 0.0455 ± 0.0192 | 0.0261 ± 0.00665 | 0.0179 ± 0.00321 |
| % Reduction of maximum peak flux while agitating | – | 42.5 (p = 0.1249) | 60.6 (p = 0.05804) |
| Total emission during 3 min agitation, (mg·m⁻²) | 6.36 ± 1.23 | 1.88 ± 0.625 | 2.12 ± 0.433 |
| % Reduction of total emissions during 3 min agitation | – | 70.4 (p < 0.0001) | 66.6 (p < 0.0001) |

2.4. Gaseous Emissions Post-Agitation (Stage 3)

Once the agitation stopped, the concentrations of H₂S started to decrease for both HAP and RO biochar treatments (Figures A1 and A2). The H₂S concentrations were recorded until they reached the levels before agitation and were stable. Both the 6 mm and 12 mm RO biochar treatment significantly (p < 0.0001) reduced cumulative H₂S emissions by 84.7% and 39.3%, respectively (Table 5).

Table 5. RO biochar treatment: the average flux and cumulative H₂S emission after agitation (bold font signifies statistical significance).

| RO Biochar after the 3 min of Agitation | Control | 12 mm Biochar | 6 mm Biochar |
|----------------------------------------|---------|---------------|--------------|
| Duration (min)                         | 36      | 36            | 36           |
| Average emissions ¹ (mg·m⁻²·min⁻¹)     | 1.37 ± 0.175 | 0.831 ± 0.0483 | 0.209 ± 0.00174 |
| Cumulative emissions ² (mg·m⁻²)        | 49.2 ± 2.63 | 29.9 ± 1.74   | 7.52 ± 0.627  |
| % Reduction of cumulative emissions    | –       | 39.3 (p < 0.0001) | 84.7 (p < 0.0001) |

¹ the average emissions were calculated using the cumulative emissions divided by the duration. ² the cumulative emissions were calculated based on the same period (post-agitation) (Figure A1).

For HAP biochar treatments, the 6 mm biochar treatment significantly (p < 0.0001) reduced cumulative emissions of H₂S by 64.4%. The 12 mm biochar treatment reduced the cumulative H₂S emissions by 17.9%, yet the reduction was not significant (p = 0.2897) (Table 6).

Table 6. HAP biochar treatment: the average flux and cumulative H₂S emission after agitation (bold font signifies statistical significance).

| HAP Biochar after the 3 min of Agitation | Control | 12 mm Biochar | 6 mm Biochar |
|----------------------------------------|---------|---------------|--------------|
| Duration (min)                         | 14      | 14            | 14           |
| Average emissions ¹ (mg·m⁻²·min⁻¹)     | 1.00 ± 0.134 | 0.821 ± 0.0936 | 0.356 ± 0.0379 |
| Cumulative emissions ² (mg·m⁻²)        | 14.0 ± 1.88 | 11.5 ± 1.31   | 4.99 ± 0.531  |
| % Reduction of cumulative emissions    | –       | 17.9 (p = 0.2897) | 64.4 (p < 0.0001) |

¹ the average emissions were calculated using the cumulative emissions divided by the duration. ² the cumulative emissions were calculated based on the same period (post-agitation) (Figure A2).
The $H_2S$ in the headspace of RO treated manure needed longer to return to the initial state compared with the HAP treatment. The $H_2S$ release was higher in the experiment testing the RO treatment (Figure A1) compared with the experiment testing the HAP treatment (Figure A2). The control concentrations exceeded the limitations of the $H_2S$ sensor. The apparent difference in the control concentrations is the result of the differences in manure used in RO and HAP experiments, that is, collected at the same farm, yet at two different times for the RO and HAP trials.

### 2.5. Kinetics of the Post-Agitation Emissions of $H_2S$

The kinetics modeling allowed further evaluation of the effect of biochar type and the dose. The $E_0$ parameter shows the potential of $H_2S$ emission during an ‘infinite’ time. The cumulative emission during the post-agitation showed that there was no ($p > 0.05$) significant influence of the HAP biochar treatment on the potential maximum cumulative flux (Figure 3). However, the lack of the significance of the differences may be caused by high variability, while still, the apparent potential for lower emission is visible. The RO application of biochar significantly ($p = 0.0086$) reduced the potential of the maximum cumulative emission in the case of the 6 mm dose; however, there were no differences between the biochar dose (Figure 3, Table A1—Appendix B). For both the RO and HAP biochar, the lowest values of $E_0$ were determined for 6 mm biochar thickness, implying that a low biochar dose could be just as effective.

![Figure 3](image-url)

**Figure 3.** The differences between the maximum cumulative $H_2S$ flux per biochar type and dose (thickness of the biochar layer). Letters indicate the significant difference within the same group of biochar types; asterisks indicate significant differences between biochar dose (Table A1). RO, red oak.

The $k$ constant presents the rate of $H_2S$ emission. The treatment by application of both types of biochar did not significantly influence ($p > 0.05$) the $k$ constant (Figure 4, Table A2—Appendix B). The lack of significant differences could be caused by high values of the standard deviations. However, the influence of the biochar dose was observed only in the case of HAP, where the 12 mm biochar reduced the $k$ value.
The k constant presents the rate of H$_2$S emission. The treatment by application of both types of biochar did not significantly influence ($p > 0.05$) the inflection time of the H$_2$S emission (Figure 5, Table A3). The lack of significant differences could be caused by high variability. However, in this case, the lowest $a_1$ values were observed for 6 mm for both biochar types.

![Figure 4](image1.png)

**Figure 4.** The differences between H$_2$S emission constant rates per the type and dose (thickness of the layer) of biochar. Letters indicate the significant difference within the same group of biochar types; asterisks indicate significant differences between thicknesses of the biochar layers (Table A2).

The $a_1$ parameter, the inflection time of the cumulative H$_2$S emission curve, represents the moment when the emission rate starts to ‘slow’ down. Similar to the k parameter, the treatment by the application of both types of biochar did not significantly influence ($p > 0.05$) the inflection time of the H$_2$S emission (Figure 5, Table A3). The lack of significant differences could be caused by high variability. However, in this case, the lowest $a_1$ values were observed for 6 mm for both biochar types.

![Figure 5](image2.png)

**Figure 5.** The differences between the inflection time of the cumulative H$_2$S emission per biochar type and the dose (thickness of the layer). Letters indicate the significant difference within the same group of biochar types; asterisks indicate significant differences between biochar dose (Table A3).
3. Discussion

Biochar treatments have the potential to reduce the risk of inhalation exposure to H$_2$S. Both 6 and 12 mm biochar treatments reduced the peak H$_2$S concentrations below the General Industrial Peak Limit (OSHA PEL, 50 ppm). The 6 mm biochar treatments, both HAP and RO, reduced the H$_2$S concentrations below the General Industry Ceiling Limit (OSHA PEL, 20 ppm) (Figures A3 and A4).

This proof-of-the-concept study shows that biochar has the potential to be an effective treatment of short-term releases of H$_2$S during and post-agitation of swine manure. From the kinetics of the post-agitation H$_2$S emissions analysis, only RO biochar has shown the significant ($p = 0.0086$) reductions on the maximum cumulative emission ($E_0$). Further, the smaller dosage (6 mm) worked just as well as the 12 mm dosage. The pH value of HAP was 9.2, while the RO pH was 7.5 [17]. It has been expected that HAP (more alkalic) would have a greater influence on H$_2$S emissions mitigation, owing to H$_2$S transformation into S$^{2-}$ ions. Previously, we have found that HAP had a stronger influence on the water pH increase than RO [17]. The apparent absence of the differences between RO and HAP in the present experiment, and even (numerically) better performance of RO biochar, could be caused by the different buffering capacity of the manure used for the experiment [18]. However, the comparison between these two types of biochars was not the aim of the study.

Biochar treatments did not have much impact on the constant emission rate ($k$) owing to the high standard deviations, except for the 12 mm HAP biochar treatment. The high variations could be caused by high heterogenicity of the stored manure properties (i.e., stratified, biologically-active, not a well-mixed solution, with local solids aggregates, and zones with different chemical properties). Therefore, one possible solution is to work with artificial surrogate manure (if a particular mechanism behind the mitigation needs to be isolated). The inflection time ($a_1$) of the cumulative emissions was not influenced much by either type of biochar; the lowest $a_1$ values were observed for 6 mm for both biochar types, where the emission rate started to slow down after 4–5 min. These findings still need to be proven on a larger scale and optimized. Still, this initial work has implications that could potentially save people and livestock lives and reduce inhalation risks during routine seasonal manure agitation, pump-out, and land application. With further research, the optimal biochar type, dose, and form of application (e.g., pellets instead of powder), it could become an effective adsorptive ‘barrier’ to protect farmers, neighbors, and livestock from harmful gases and odors emitted from manure.

Surprisingly, the 6 mm biochar treatment was a numerically more effective dosage because the % reduction was slightly higher while using less biochar. The smaller amount of biochar used has an immediate impact and economics and on the feasibility of technology adoption. When the biochar is wetted, it forms ‘chunks’. When manure is being agitated, the bigger chunks of biochar in 12 mm treatments started to turn over, sink, and mix with manure much faster than with the 6 mm dose. Once the physical barrier on the surface was broken, the maximum concentration of the treatment began to rise and was closer to the Control.

In future research, other kinds of biochar could be tested for their efficacy to mitigate gaseous emissions from manure. The effects of the dose and frequency of application of commercial biochars, functionalized biochars, pelletized biochar, as well as the synergy between gaseous emissions and agronomic benefits to soil should be tested. Additionally, farm-scale research is also required for the proof-of-the-concept. With more extensive farm-scale trials, researchers should consider how and where the biochar could be practically applied in order to create an effective short-term barrier to maximize the benefit of biochar treatment. Application of powdery, light, and dusty material might be hazardous itself and not be feasible in farm conditions. Pelletized biochar could be a more practical and safer mode of application. Opportunities exist to mitigate other types of gases and other applications (e.g., industrial wastewater, compost, landfill leachate) with biochar.
4. Experiments

4.1. Manure, Biochars, H$_2$S Measurements

Fresh manure was collected twice from deep-pit storage at a local swine farm in central Iowa. The manure treated with the red oak (RO) biochar was collected in summer, whereas manure treated with the highly alkaline and porous (HAP) biochar was collected in winter. Thus, the experimental design was set up to compare the Treatment and Control of the same type of biochar. The manure properties and, therefore, baseline H$_2$S concentrations for control groups were different for HAP and RO trials. The proof-of-the-concept simulation of the deep pit and agitation was facilitated by 1.22 m (height) and 0.38 m (diameter) manure storage. The working volume of the manure was 103.1 L, while the headspace was ventilated with 7.5 air exchanges per hour (ACH), which is representative of the ventilation of deep-pit manure storage [11,26]. A 1/10 hp transfer pump (Little Giant, Fort Wayne, IN) was used to agitate the manure with a 1.36 m$^3$ h$^{-1}$ flow rate.

Biochar physicochemical properties were described elsewhere [16–18]. Briefly, some key properties are listed below. RO biochar was pyrolyzed at 500–550 °C. It had a pH of 7.5 and a 6.75 zero-point charge, consisting of C (78.53% dry matter, d.m.), H (2.54% d.m.), N (0.62% d.m.), and volatile solids (VS, 26.38% d.m.). Fixed C and ash were 54.76% and 15.83% d.m., respectively [16–18]. The HAP biochar was made from corn stover pyrolyzed at 500 °C. The pH was 9.2 and 8.42 zero-point charge, consisting of C (61.37% d.m.), H (2.88% d.m.), N (1.21% d.m.), and VS (16.27% d.m.). Fixed C and ash were 34.98% and 46.82% d.m., respectively [16–18].

OMS-300 real-time monitoring system equipped with electrochemical gas sensors (H$_2$S/C-50) (Smart Control & Sensing Inc., Daejeon, Korea) was used to measure the real-time H$_2$S concentration [27,28]. The analyzer was calibrated with standard gas before use [27,28].

4.2. Experimental Design

The pilot-scale setup was simulating deep pit swine manure storage while manure was being agitated (Figure 6). The inlet of the pump was connected to the bottom manure sampling port; the outlet was connected to the middle manure sampling port. During agitation, the manure was pumped from the bottom to the middle zone for 3 min. Three variants per each biochar and each with triplicates experiments:

- Manure not treated with biochar—control variant.
- Manure treated with—6 mm thick layer of biochar.
- Manure treated with—12 mm thick layer of biochar.

The biochar dose was based on its volume spread over the manure surface, resulting in either 6 or 12 mm average thicknesses. The headspace H$_2$S concentrations were measured in the exhaust (Figure 6) continuously during the following stages:

- Stage 1: No agitation. Post biochar application and pre-agitation for all three variants.
- Stage 2: Agitation. All three variants during agitation.
- Stage 3: Post-agitation. All three variants after agitation until the headspace H$_2$S concentration reached its initial state.
4.3. Data Analysis, the Kinetics of Emissions

The mitigation effect was estimated by comparing measured emissions associated with the Control (not treated) and treatment (treated with biochar) manure. The % reduction was calculated as the percent ratio of (control – treatment)/control.

The one-way analysis of variance (ANOVA) and Tukey–Kramer method in JMP software (version Pro 14, SAS Institute, Inc., Cary, NC, USA) were used to analyze the data to determine the p-values of total emissions for both overall and during 3 min. The maximum levels of concentrations were used for a pooled T-test to estimate the p-values. A p-value < 0.05 was used as a statistical significance threshold. The Gompertz model was used for the determination of the post-agitation cumulative H$_2$S emission kinetics [29]:

$$E = E_0 e^{(-e^{-k(t-a_1)})}$$

where $E$—H$_2$S emission flux, mg.m$^{-2}$; $E_0$—H$_2$S maximum cumulative emission flux, mg m$^{-2}$; $k$—constant rate of the H$_2$S emission flux, s$^{-1}$; $t$—time, s; and $a_1$—the inflection time of the cumulative H$_2$S emission, s.

The non-linear regression was used for the determination of the cumulative emission kinetics with the application of the Statistical 13 software (TIBCO Software Inc., Palo Alto, CA, USA). The R$^2$ determination coefficient was estimated to indicate the fitting the model to data. The kinetic analysis was completed for each variant and each repetition. The result of the regression analysis for each variant is provided in Appendix A (Figures A5–A22) and used to estimate the average values of $E_0$, $k$, and $a_1$ (Equation (1)). The ANOVA test was applied with post-hoc Tukey’s test to indicate the statistical significance ($p < 0.05$) of the differences between average values. The calculated probabilities of Tukey’s test are given in Appendix B.

5. Conclusions

The highly alkaline and porous (HAP) and red oak (RO) biochar treatments have the potential to reduce the risk of inhalation exposure to H$_2$S. Both the 6 mm and 12 mm RO biochar treatment
significantly ($p < 0.0001$) reduced the total emission of H$_2$S by 67.4% and 62.4%, respectively. The 6 mm and 12 mm RO biochar treatment resulted in a 63.0% ($p = 0.0511$) and 23.6% ($p = 0.145$) reduction in the maximum peak flux of H$_2$S, respectively. Both the 6 mm and 12 mm HAP biochar treatment significantly ($p < 0.0001$) reduced the total emission of H$_2$S by 66.6% and 70.4%, respectively. The 6 mm and 12 mm RO biochar treatment resulted in 60.6% ($p = 0.05804$) and 42.5% ($p = 0.1249$) reduction in the maximum peak flux of H$_2$S, respectively. Both 6 and 12 mm biochar treatments reduced the peak H$_2$S concentrations below the General Industrial Peak Limit (OSHA PEL, 50 ppm). The 6 mm biochar treatments reduced the H$_2$S concentrations below the General Industry Ceiling Limit (OSHA PEL, 20 ppm). Research scaling up to larger manure volumes and longer agitation is warranted.

**Author Contributions:** Conceptualization, J.A.K. and B.C.; methodology, B.C. and J.A.K.; software, B.C. and A.B.; validation, J.A.K. and A.B.; formal analysis, B.C.; investigation, B.C., M.L., H.M., P.L. and Z.M.; resources, J.A.K. and R.C.B.; data curation, B.C., J.A.K. and A.B.; writing—original draft preparation, B.C.; writing—review and editing, J.A.K. and A.B.; visualization, B.C., H.M., and A.B.; supervision, J.A.K. and A.B.; project administration, J.A.K. and R.C.B.; funding acquisition, J.A.K. and R.C.B. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was partially funded by the U.S. Department of Energy—National Institute for Food and Agriculture, grant # 2018-10008-28616: ‘Valorization of biochar: Applications in anaerobic digestion and livestock odor control (2018–2020, PI R.B.). In addition, this research was partially supported by the Iowa Agriculture and Home Economics Experiment Station, Ames, Iowa. Project no. IOW05556 (Future Challenges in Animal Production Systems: Seeking Solutions through Focused Facilitation) sponsored by Hatch Act and State of Iowa funds. The authors would like to thank the Ministry of Education and Science of the Republic of Kazakhstan for supporting Z.M. with an M.S. study scholarship via the Bolashak Program. Authors would like to thank the Fulbright Poland Foundation for funding the project titled “Research on pollutants emission from Carbonized Refuse Derived Fuel into the environment,” completed by A.B. at the Iowa State University. The authors would like to express gratitude to Samuel O’Brien for his helpful corrections to grammar.

**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

**Appendix A**

![Figure A1](image-url). The short-term H$_2$S emissions when manure is treated surficially with RO biochar layer at two thicknesses (6 mm; 12 mm) immediately prior to 3 min agitation. Each data point is the average of triplicate, and the error bar signifies a standard deviation.
Figure A2. The short-term H$_2$S emissions when manure is treated surficially with HAP biochar layer at two thicknesses (6 mm; 12 mm) immediately prior to 3 min agitation. Each data point is the average of triplicate, and the error bar signifies a standard deviation.

Figure A3. The short-term H$_2$S concentrations when manure is treated surficially with HAP biochar layer at two thicknesses (6 mm; 12 mm) immediately prior to 3 min agitation. Each data point is the average of triplicate, and the error bar signifies a standard deviation. Red line = the ‘General Industry Peak Limit’ (OSHA PEL = 50 ppm); yellow line = the ‘General Industry Ceiling Limit’ (OSHA PEL = 20 ppm) [1].
**Figure A4.** The short-term H$_2$S concentrations when manure is treated surficially with RO biochar layer at two thicknesses (6 mm; 12 mm) immediately prior to 3 min agitation. Each data point is the average of triplicate, and the error bar signifies a standard deviation. Red line = the ‘General Industry Peak Limit’ (OSHA PEL = 50 ppm); yellow line = the ‘General Industry Ceiling Limit’ (OSHA PEL = 20 ppm) [1].

**Figure A5.** The cumulative H$_2$S flux. Variant with no HAP biochar, repetition 1. Gompertz equation parameters and R$^2$ determination coefficient.

**Figure A6.** The cumulative H$_2$S flux. Variant with no HAP biochar, repetition 2. Gompertz equation parameters and R$^2$ determination coefficient.
Figure A6. The cumulative H$_2$S flux. Variant with no HAP biochar, repetition 2. Gompertz equation parameters and $R^2$ determination coefficient.

Figure A7. The cumulative H$_2$S flux. Variant with no HAP biochar, repetition 3. Gompertz equation parameters and $R^2$ determination coefficient.

Figure A8. The cumulative H$_2$S flux. Variant with 12 mm HAP biochar layer, repetition 1. Gompertz equation parameters and $R^2$ determination coefficient.

Figure A9. The cumulative H$_2$S flux. Variant with 12 mm HAP biochar layer, repetition 2. Gompertz equation parameters and $R^2$ determination coefficient.
Figure A9. The cumulative H$_2$S flux. Variant with 12 mm HAP biochar layer, repetition 2. Gompertz equation parameters and R$^2$ determination coefficient.

Figure A10. The cumulative H$_2$S flux. Variant with 12 mm HAP biochar layer, repetition 3. Gompertz equation parameters and R$^2$ determination coefficient.

Figure A11. The cumulative H$_2$S flux. Variant with 6 mm HAP biochar layer, repetition 1. Gompertz equation parameters and R$^2$ determination coefficient.

Figure A12. The cumulative H$_2$S flux. Variant with 6 mm HAP biochar layer, repetition 2. Gompertz equation parameters and R$^2$ determination coefficient.
Figure A12. The cumulative H$_2$S flux. Variant with 6 mm HAP biochar layer, repetition 2. Gompertz equation parameters and R$^2$ determination coefficient.

Figure A13. The cumulative H$_2$S flux. Variant with 6 mm HAP biochar layer, repetition 3. Gompertz equation parameters and R$^2$ determination coefficient.

Figure A14. The cumulative H$_2$S flux. Variant with no RO biochar, repetition 1. Gompertz equation parameters and R$^2$ determination coefficient.

Figure A15. The cumulative H$_2$S flux. Variant with no RO biochar, repetition 2. Gompertz equation parameters and R$^2$ determination coefficient.
Figure A15. The cumulative H$_2$S flux. Variant with no RO biochar, repetition 2. Gompertz equation parameters and $R^2$ determination coefficient.

Figure A16. The cumulative H$_2$S flux. Variant with no RO biochar, repetition 3. Gompertz equation parameters and $R^2$ determination coefficient.

Figure A17. The cumulative H$_2$S flux. Variant with 12 mm RO biochar layer, repetition 1. Gompertz equation parameters and $R^2$ determination coefficient.

Figure A18. The cumulative H$_2$S flux. Variant with 12 mm RO biochar layer, repetition 2. Gompertz equation parameters and $R^2$ determination coefficient.
Figure A18. The cumulative H$_2$S flux. Variant with 12 mm RO biochar layer, repetition 2. Gompertz equation parameters and R$^2$ determination coefficient.

Figure A19. The cumulative H$_2$S flux. Variant with 12 mm RO biochar layer, repetition 3. Gompertz equation parameters and R$^2$ determination coefficient.

Figure A20. The cumulative H$_2$S flux. Variant with 6 mm RO biochar layer, repetition 1. Gompertz equation parameters and R$^2$ determination coefficient.

Figure A21. The cumulative H$_2$S flux. Variant with 6 mm RO biochar layer, repetition 2. Gompertz equation parameters and R$^2$ determination coefficient.
Figure A21. The cumulative H$_2$S flux. Variant with 6 mm RO biochar layer, repetition 2. Gompertz equation parameters and $R^2$ determination coefficient.

Figure A22. The cumulative H$_2$S flux. Variant with 6 mm RO biochar layer, repetition 3. Gompertz equation parameters and $R^2$ determination coefficient.

Appendix B

Table A1. Tukey’s HSD test; variable: maximum cumulative H$_2$S flux (mg·m$^{-2}$). Differences marked with red font are significant ($p < 0.05$).

| Biochar | HAP | HAP | HAP | RO | RO | RO |
|---------|-----|-----|-----|----|----|----|
|         | The Thickness of the Biochar Layer | 6 | 12 | No Biochar | 6 | 12 | No Biochar |
| HAP     | 6   | 0.971979 | 0.931431 | 0.999902 | 0.186020 | 0.005935 |
| HAP     | 12  | 0.971979 | 0.999963 | 0.994297 | 0.500670 | 0.020403 |
| HAP No biochar | 0.931431 | 0.999963 | 0.977866 | 0.604926 | 0.027845 |
| RO      | 6   | 0.999902 | 0.942979 | 0.977866 | 0.258371 | 0.008562 |
| RO      | 12  | 0.186020 | 0.500670 | 0.604926 | 0.258371 | 0.351435 |
| RO No biochar | 0.005935 | 0.020403 | 0.027845 | 0.008562 | 0.351435 |

Table A2. Tukey’s HSD test; variable: H$_2$S emission constant rate (s$^{-1}$). Differences marked with red font are significant ($p < 0.05$).

| Biochar | HAP | HAP | HAP | RO | RO | RO |
|---------|-----|-----|-----|----|----|----|
|         | The Thickness of the Biochar Layer | 6 | 12 | No Biochar | 6 | 12 | No Biochar |
| HAP     | 6   | 0.637682 | 0.999840 | 0.061820 | 0.042644 | 0.031894 |
| HAP     | 12  | 0.637682 | 0.496960 | 0.570706 | 0.448007 | 0.362320 |
| HAP No biochar | 0.999840 | 0.496960 | 0.040832 | 0.028090 | 0.020990 |
| RO      | 6   | 0.061820 | 0.570706 | 0.040832 | 0.999907 | 0.998455 |
| RO      | 12  | 0.042644 | 0.448007 | 0.028090 | 0.999907 | 0.999973 |
| RO No biochar | 0.031894 | 0.362320 | 0.020990 | 0.998455 | 0.999973 |

Table A3. Tukey’s HSD test; variable: The inflection time of the cumulative H$_2$S emission (s). Differences marked with red font are significant ($p < 0.05$).

| Biochar | HAP | HAP | HAP | RO | RO | RO |
|---------|-----|-----|-----|----|----|----|
|         | The Thickness of the Biochar Layer | 6 | 12 | No Biochar | 6 | 12 | No Biochar |
| HAP     | 6   | 0.762503 | 0.998558 | 0.977229 | 0.038806 | 0.068427 |
| HAP     | 12  | 0.762503 | 0.543358 | 0.986994 | 0.314408 | 0.479691 |
| HAP No biochar | 0.998558 | 0.543358 | 0.873116 | 0.020139 | 0.035707 |
| RO      | 6   | 0.977229 | 0.986894 | 0.873116 | 0.124583 | 0.209978 |
| RO      | 12  | 0.038806 | 0.314408 | 0.020139 | 0.124583 | 0.999261 |
| RO No biochar | 0.068427 | 0.479691 | 0.035707 | 0.209978 | 0.999261 |
References

1. OSHA. 29 CFR 1910.1000, Table Z-2: Toxic and Hazardous Substances; Occupational Safety and Health Administration: Washington, DC, USA, 2017.

2. Ni, J.Q.; Heber, A.J.; Sutton, A.L.; Kelly, D.T. Mechanisms of gas releases from swine wastes. *Trans. ASABE* 2009, 52, 2013–2025. [CrossRef]

3. Alowairdi, L. Teenager Killed in farm accident in Clark County. 2016. Available online: https://www.weau.com/content/news/Teenager-killed-in-farm-accident-in-Clark-County-393467341.html (accessed on 9 July 2020).

4. Ballerino-Regan, D.; Longmire, A.W. Hydrogen sulfide exposure as a cause of sudden occupational death. *Arch. Pathol. Lab. Med.* 2010, 134, 1105. [PubMed]

5. Salem, O.H. OSHA: Ohio Farm Worker Killed by Manure Gas. 2016. Available online: https://www.farmanddairy.com/news/osha-ohio-farm-worker-killed-by-manure-gas/328366.html (accessed on 9 July 2020).

6. Mueller, C. Coroner: Farmer Died of Gas Poisoning. 2016. Available online: http://www.stevenspointjournal.com/story/news/2016/09/14/coroner-farmer-died-gaspoisoning/90365328/?hootPostID=116e126a90c5dabc8fb7604ef6f01d17 (accessed on 9 July 2020).

7. Maurer, D.L.; Koziel, J.A.; Harmon, J.D.; Hoff, S.J.; Rieck-Hinz, A.M.; Andersen, D.S. Summary of performance data for technologies to control gaseous, odor, and particulate emissions from livestock operations: Air management practices assessment tool (AMPAT). *Data Brief* 2016, 7, 1413–1429. [CrossRef] [PubMed]

8. Maurer, D.L.; Koziel, J.A.; Kalus, K.; Anderson, D.S.; Opalinski, S. Pilot-Scale Testing of Non-Activated Biochar for Swine Manure Treatment and Mitigation of Ammonia, Hydrogen Sulfide, Odorous Volatile Organic Compounds (VOCs) and Greenhouse Gas Emissions. *Sustainability* 2017, 9, 929. [CrossRef]

9. Parker, D.B.; Hayes, M.; Brown-Brandl, T.; Woodbury, B.L.; Spiehs, M.J.; Koziel, J.A. Surface application of soybean peroxidase and calcium peroxide for reducing odorous VOC emissions from swine manure slurry. *Appl. Eng. Agric.* 2016, 32, 389–398. [CrossRef]

10. Maurer, D.L.; Koziel, J.A.; Bruning, K.; Parker, D.B. Farm-scale testing of soybean peroxidase and calcium peroxide for surficial swine manure treatment and mitigation of odorous VOCs, ammonia and hydrogen sulfide emissions. *Atmos. Environ.* 2017, 166, 467–478. [CrossRef]

11. Maurer, D.L.; Koziel, J.A.; Bruning, K.; Parker, D.B. Pilot-scale testing of renewable biocatalyst for swine manure treatment and mitigation of odorous VOCs, ammonia and hydrogen sulfide emissions. *Atmos. Environ.* 2017, 150, 313–321. [CrossRef]

12. Cai, L.; Koziel, J.A.; Liang, Y.; Nguyen, A.T.; Xin, H. Evaluation of zeolite for Control of odorants emissions from simulated poultry manure storage. *J. Environ. Qual.* 2007, 36, 184–193. [CrossRef]

13. Kalus, K.; Opalinski, S.; Maurer, D.; Rice, S.; Koziel, J.A.; Korczyński, M.; Dobrzański, Z.; Kołacz, R.; Gutarowska, B. Odour reducing microbial-mineral additive for poultry manure treatment. *Front. Environ. Sci. Eng.* 2017, 11, 7. [CrossRef]

14. Chen, B. Evaluating the Effectiveness of Manure Additives on Mitigation of Gaseous Emissions from Deep Pit Swine Manure. Master’s Thesis, Iowa State University, Ames, IA, USA, 2019.

15. Chen, B.; Koziel, J.A.; Banik, C.; Ma, H.; Lee, M.; Meiirkhanuly, Z.; Andersen, D.S.; Białowiec, A.; Parker, D.B. Emissions from Swine Manure Treated with Current Products for Mitigation of Odors and Reduction of NH₃, H₂S, VOC, and GHG Emissions. *Data* 2020, 5, 54. [CrossRef]

16. Meiirkhanuly, Z.; Koziel, J.A.; Białowiec, A.; Banik, C.; Chen, B.; Lee, M.; Wi, J.; Brown, R.C.; Bakshi, S. Mitigation of gaseous emissions from swine manure with biochar. In Proceedings of the 2020 ASABE Annual International Meeting, Omaha, NE, USA, 13–15 July 2020. [CrossRef]

17. Meiirkhanuly, Z.; Koziel, J.A.; Białowiec, A.; Banik, C.; Brown, R.C. The-Proof-of-Concept of Biochar Floating Cover Influence on Water pH. *Water* 2019, 11, 1802. [CrossRef]

18. Meiirkhanuly, Z.; Koziel, J.A.; Białowiec, A.; Banik, C.; Brown, R.C. The proof-of-the-concept of biochar floating cover influence on swine manure pH: Implications for mitigation of gaseous emissions from area sources. *Front. Chem.* 2020. [CrossRef]

19. Białowiec, A.; Micuda, M.; Koziel, J.A. Waste to Carbon: Densification of Torrefied Refuse-Derived Fuel. *Energies* 2018, 11, 3233. [CrossRef]
20. Stępień, P.; Święchowski, K.; Hnat, M.; Kugler, S.; Stegenta-Dąbrowska, S.; Koziel, J.A.; Manczarski, P.; Białowiec, A. Waste to Carbon: Biocoal from Elephant Dung as New Cooking Fuel. *Energies* 2019, 12, 4344. [CrossRef]

21. Pulka, J.; Manczarski, P.; Koziel, J.A.; Białowiec, A. Torrefaction of Sewage Sludge: Kinetics and Fuel Properties of Biochars. *Energies* 2019, 12, 565. [CrossRef]

22. Święchowski, K.; Stegenta-Dąbrowska, S.; Liszewski, M.; Bąbelewski, P.; Koziel, J.A.; Białowiec, A. Oxytree Pruned Biomass Torrefaction: Process Kinetics. *Materials* 2019, 12, 3334. [CrossRef] [PubMed]

23. Stępień, P.; Serowik, M.; Koziel, J.A.; Białowiec, A. Waste to carbon: Estimating the demand for production of carbonized refuse-derived fuel. *Sustainability* 2019, 11, 5685. [CrossRef]

24. Sygula, E.; Koziel, J.A.; Białowiec, A. Proof-of-Concept of Spent Mushrooms Compost Torrefaction—Studying the Process Kinetics and the Influence of Temperature and Duration on the Calorific Value of the Produced Biocoal. *Energies* 2019, 12, 3060. [CrossRef]

25. Kalus, K.; Koziel, J.A.; Opaliński, S. A Review of Biochar Properties and Their Utilization in Crop Agriculture and Livestock Production. *Appl. Sci.* 2019, 9, 3494. [CrossRef]

26. MidWest Plan Service. *Structures and Environment Handbook*, 11th ed.; Midwest Plan Service: Ames, IA, USA, 1983; ISBN 0-89373-057-2.

27. Wi, J.; Lee, S.; Kim, E.; Lee, M.; Koziel, J.A.; Ahn, H. Evaluation of Semi-Continuous Pit Manure Recharge System Performance on Mitigation of Ammonia and Hydrogen Sulfide Emissions from a Swine Finishing Barn. *Atmosphere* 2019, 10, 170. [CrossRef]

28. Lee, M.; Wi, J.; Koziel, J.A.; Ahn, H.; Li, P.; Chen, B.; Meirkhanuly, Z.; Banik, C.; Jenks, W. Effects of UV-A Light Treatment on Ammonia, Hydrogen Sulfide, Greenhouse Gases, and Ozone in Simulated Poultry Barn Conditions. *Atmosphere* 2020, 11, 283. [CrossRef]

29. Hanusz, Z.; Siarkowski, Z.; Ostrowski, K. Application of the Gompertz model in agricultural engineering. *Inż. Rol.* 2008, 7, 71–77.

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).