2950 Niles Road, St. Joseph, MI 49085-9659, USA
269.429.0300 fax 269.429.3852 hq@asabe.org www.asabe.org

An ASABE Meeting Presentation
DOI: https://doi.org/10.13031/aim.202100088
Paper Number: 2100088

Removing barriers for adoption of biochar treatment to mitigate gaseous emissions from manure: can common binders improve the performance of powder and pelletized biochar?

Samuel O'Brien [1], Jacek Koziel [1], Baitong Chen [1], Ryan Ungs [2], Cail Donkersloot [2], Cameron Cimino [2], Chumki Banik [1], Eric Cochran [3]

[1]Iowa State University, Department of Agricultural and Biosystems Engineering, Ames, USA

[2]Iowa State University, Univerity Honors Program, Ames, USA

[3]Iowa State University, Department of Chemical and Biological Engineering, Ames, USA

Written for presentation at the
2021 Annual International Meeting
ASABE Virtual and On Demand
July 12–16, 2021

ABSTRACT. *Biochar is a fine carbonaceous powder byproduct that has many potential practical applications to improve the sustainability of crop and animal production systems. Our recent work showed that biochar powder as a surficial manure additive reduces the emissions of odorous volatile organic compounds (VOCs), ammonia (NH_3), and highly toxic hydrogen sulfide (H_2S) in both the short- and long term. Biochar floating on or near the manure surface improves the mitigation effect in the long-term and reduces the need for reapplication. These recent discoveries improve the potential to mitigate gaseous emissions and the sustainability of manure as a fertilizer. We identified one practical barrier to adopting this technology on a farm scale. Biochar powder can be difficult to store, transport, and apply. We hypothesized that combining biochar treatment with other biomass-derived products and/or pelletizing biochar with common and abundant binders (water, wax, soybean-based epoxy) improves the practical aspects of emissions treatment. The objective was to determine raw biochar, soybean-derived epoxy (BioMAG), and biochar pellets' (made with a combination of water, wax, and BioMAG) ability to float in water. This research was conducted in two stages. First, we tested the floatability of raw (powder) biochar, BioMAG, and biochar layered on BioMAG). The second stage tested the biochar pellets made with water, wax, and BioMAG. All tests were completed in triplicates using red oak biochar. Preliminary observations confirmed the potential for improving biochar floatability in both powder and pelletized forms. A layer of soybean-based epoxy can support raw biochar powder and improve its floatability. The best treatment was the layered BioMAG (6.5 mm) with 6.5 mm of biochar on top that stayed afloat for at least 9 days. Also, biochar powder was held together with combinations of binders and made into pellets with improved application potential. The best pellet treatment was composed of 70% biochar, 15% water, and 15% wax. This mix of biochar and binders stayed afloat for at least 9 days. Both successful results warrant further research and trials of the best treatments to mitigate gaseous emissions from manure. The results of this research are needed for scaling up the surficial treatment of stored manure with biochar powder and pellets on the pilot- and farm-scales.*

Keywords: *air quality, ammonia, animal agriculture, biocoal, livestock manure, odor, waste management, sustainability.*

Introduction

Recent discoveries show that biochar is synergistically capable of solving two major challenges in animal-crop production systems (Banik et al., 2021a, 2021b). First, biochar treatment can mitigate gaseous emissions from manure. Then, the manure-biochar mixture is applied to the soil to reduce the risk of nutrient run-off (Banik et al., 2021a) and improve agronomic metrics for corn and soybeans (Banik et al., 2021b).

A common problem in livestock production is that harmful and odorous gaseous emissions are generated during the long-term storage of animal manure (Ni et al., 2018; Chen et al., 2020a, 2020b, 2020c, 2021; Meiirkhanuly et al., 2020). Manure agitation (to stir in solids within the slurry to maintain the desired consistency) and pump out releases elevated levels of hydrogen sulfide (H_2S) and ammonia (NH_3) (NIOSH, 2017; Hoff et al., 2006). A proposed method of reducing the emission of these harmful gases is through the surficial application of biochar (Chen et al., 2021). Biochar is characterized as a fine carbonaceous powder that is very useful as a sorbent, and when layered on top of manure, can capture the release of emissions from these gas bubbles (Figure 1) (Chen et al., 2020a, 2020b, 2020c, 2021, Meiirkhanuly et al., 2020).

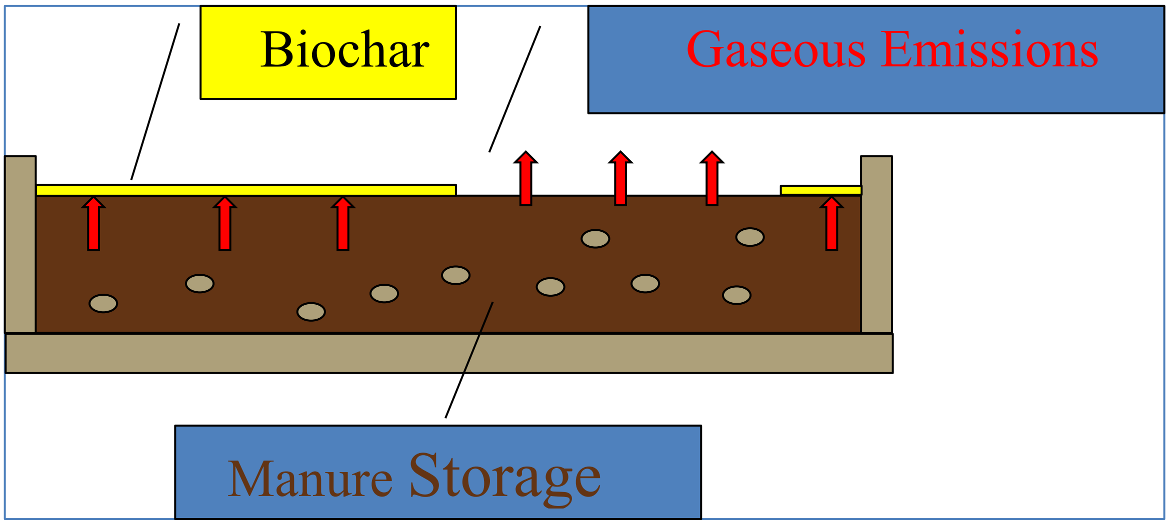

Figure 1. The concept illustration of mitigation of gaseous emissions from stored manure with the surficial application of biochar.

Biochar is the byproduct of thermal processing of biomass (Białowiec et al., 2018), has been considered for an increasing number of applications in agriculture (Kalus et al., 2019), and provides a more sustainable solution to emission reduction from manure. In raw powder form, produced directly from pyrolysis biochar can reduce the emission of H_2S by up to 60% and NH_3 by between 70-80% when applied right before 3-min manure agitation (Chen et al., 2020b; Chen et al., 2020c).

The primary issue with biochar as a surficial manure additive is the difficulty of handling and working with biochar powder. In powdered form, biochar is both very fine and lightweight. Biochar powder could be difficult to store and an impractical product to work with on a larger scale. Dust from biochar inhalation can also be hazardous. Likewise, biochar powder can self-ignite (Dzonzi-Undi et al., 2014).

Biochar floatability is the key characteristic affecting its effectiveness in mitigating gaseous emissions during long-term storage of manure. We propose that raw biochar floatability could be improved by adding other biomass-derived materials and/or by pelletizing. The pelletization can also improve the practical means of on-farm application to manure. The objective was to determine raw biochar, soybean-derived epoxy, and biochar pellets' (made with a combination of water, wax, and soybean-derived epoxy) ability to float. The results are needed to select a more practical approach to biochar application to manure where the floatability of the applied biochar-based product is critical to its success in mitigating emissions.

Materials and Methods

In this experiment, we tested the effectiveness of three binders on their effectiveness in creating a biochar pellet that would float. The biochar used was made from red oak, and the binders tested included water, melted wax, and a soybean-based epoxy called BioMAG, derived from asphalt pavement rejuvenation research (Elkashef et al., 2017).

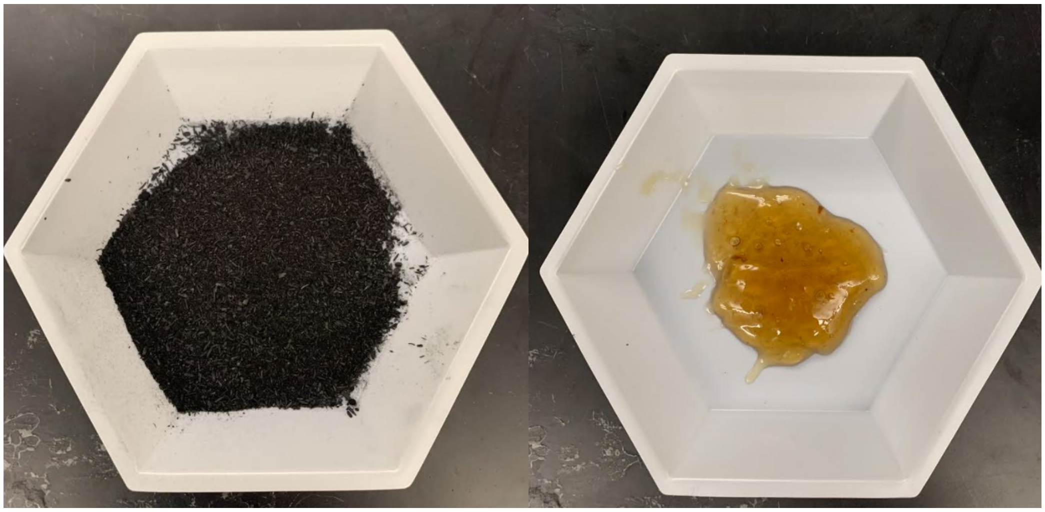

Figure 2. Biochar powder (left). Soybean-based epoxy (BioMAG) (right).

The conducted research was split into three separate experiments. The first set of trials focused on evaluating the effects of the BioMAG product to determine if it had the potential for pelletization or other potential applications combined with biochar. In this experiment, we compared the floatability of raw biochar, raw BioMAG, and biochar layered on top of BioMAG. Three distinct levels of thickness were tested, 3 mm (1/8"), 6 mm (¼"), and 13 mm (½ ") layered on water. For biochar and BioMAG combination trials, we split the total volume equally between both materials, e.g., (1.5 mm of BioMAG + 1.5 mm of biochar = 3 mm).

After the initial testing with raw materials, we proceeded with pelletization. The second and third experiments conducted each involved three scenarios and were performed using n =3 replications. The second experiment compared the floatability of the biochar pellets. Specifically, we compared pellets utilizing BioMAG as a binder with those utilizing water & BioMAG combinations. Experiment two design stemmed directly from the results of experiment one. Finally, the third experiment compared the floatability of water-based biochar pellets compared to biochar pellets made using a water and wax combination.

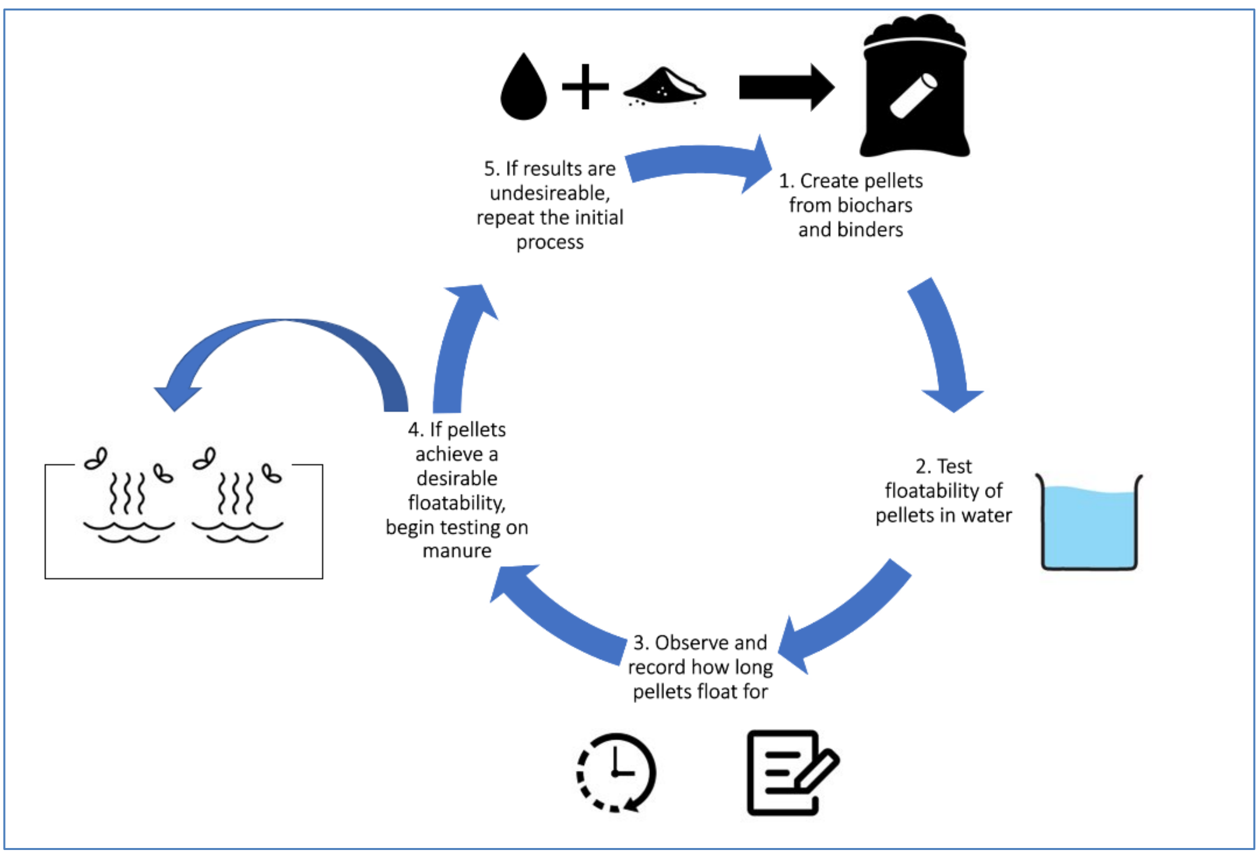

Figure 3. The process of biochar pelletization and comparing floatability for biochar pellets with biochar powder.

All pelletization was performed using a hydraulic press at 1,000 psi for 1 min. The hydraulic press was used to make biochar pellets (Figure 4).

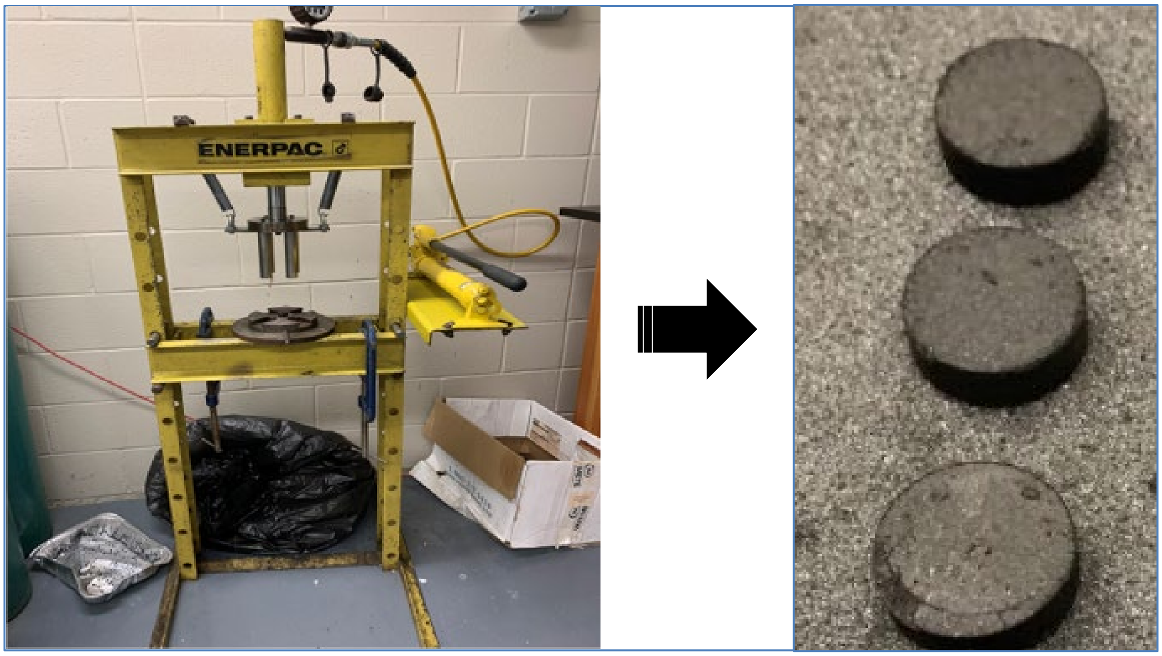

Figure 4. The hydraulic press (right) was used for making the biochar pellets (right).

Table 1. Experimental design for testing the floatability of biochar pellets.

Experiments and Corresponding Figures	Figure Contents
Experiment 1: Biochar powder vs. BioMAG vs. Layered Biochar powder and BioMAG	
Figures 5 and 6	Biochar powder, side view
Figures 7 and 8	BioMAG, side view
Figures 9 and 10	Layered Biochar powder and BioMAG, side view
Figures 11 and 12	Biochar powder, top view
Figures 13 and 14	BioMAG, top view
Figures 15 and 16	Layered Biochar powder and BioMAG, top view
Experiment 2: BioMAG vs. BioMAG/water-based pellets	
Figure 17	BioMAGvs. BioMAG/water-based pellets
Figure 18	BioMAG vs. BioMAG/water-based pellets
Figure 19	BioMAG vs. BioMAG/water-based pellets
Experiment 3: Water vs. water/wax-based pellets	
Figure 20	Water vs. water/wax-based pellets
Figure 21	Water vs. water/wax-based pellets

Results

Experiment 1: Biochar vs. BioMAG vs. Biochar with BioMAG floatability.

Floatability trials were conducted for raw biochar, raw BioMAG, and biochar layered on top of BioMAG, all applied to water. Three levels of treatment thickness were tested:

- 3 mm (1/8")
- 6 mm (¼"), and
- 13 mm (½ ") layered on water.

In the following images, the data for the 3 mm, 6 mm, and 13 mm trials are presented in the left, center, and right sides of each figure, respectively. Occasionally, images are presented vertically, in which case the left-to-right convention applies in the same manner from the top-to-down. Images are representative examples of n=3 replicates.

Side Views

a. Raw Biochar Floatability

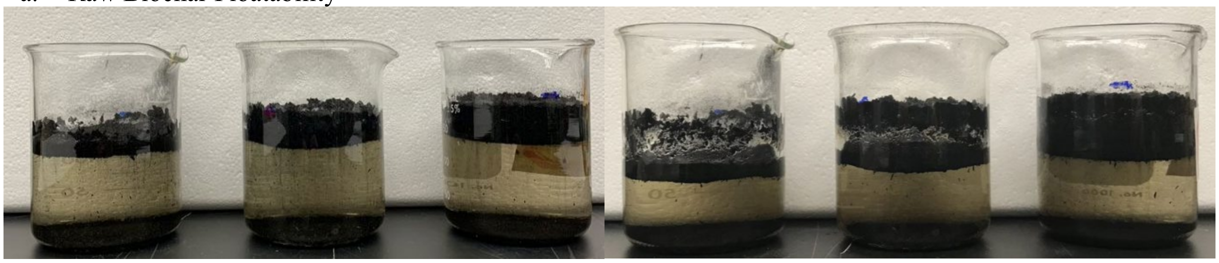

Figure 5. Biochar (100%) surficially applied to water (n = 3 replicates, the picture represents one example) (Day 1, left). Dosage per beaker from left to right: 3 mm, 6 mm, and 13 mm. Most of the biochar floats with a small fraction sunk and suspended. Significant water incorporation into biochar and evaporation occurred by Day 3 (right).

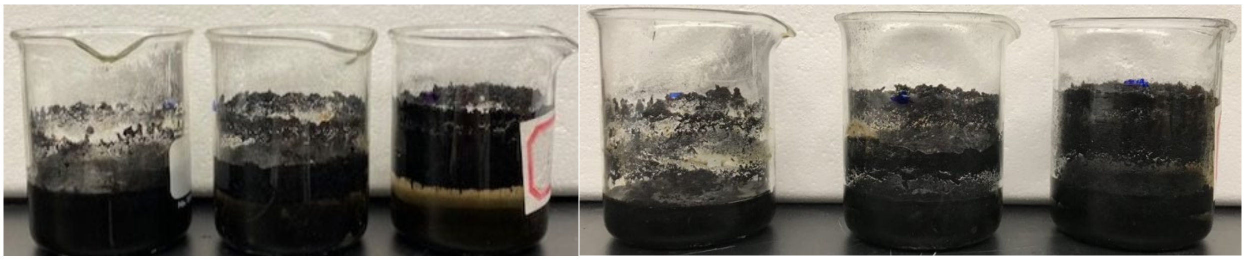

Figure 6. Biochar (100%) surficially applied to water (n = 3 replicates, the picture represents one example) (Day 7). Dosage per beaker from left to right: 3 mm, 6 mm, and 13 mm. Significant water incorporation into biochar and evaporation continued to occur. The 3 mm and 6mm treatments have lost almost all their water and have begun to settle completely by Day 9. The 13 mm treatment displays a slower rate of water incorporation/evaporation but has still mostly sunk by Day 9 (right).

b. Raw BioMAG Floatability

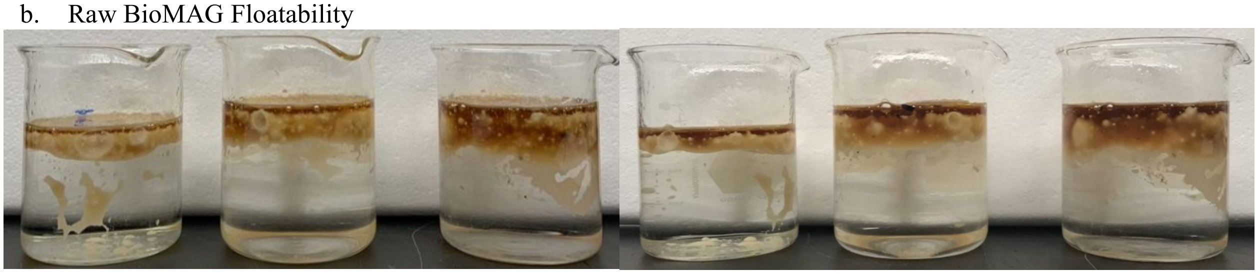

Figure 7. BioMAG is applied and spread over the water surface (n = 3 replicates, the picture represents one example). Dosage per beaker from left to right: 3 mm, 6 mm, and 13 mm. A thin darker layer formed on the top of the BioMAG by Day 3. This darker layer appeared to be is unexposed to water beneath it. Day 1 (left), Day 3 (right).

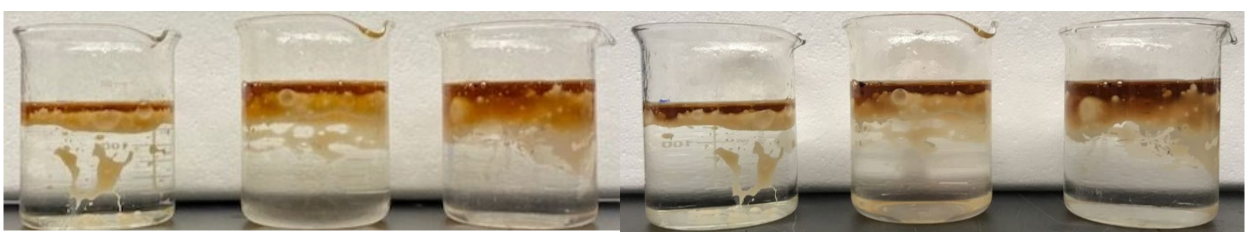

Figure 8. BioMAG applied and spread over the water surface (n = 3 replicates, the picture represents one example). Dosage per beaker from left to right: 3 mm, 6 mm, and 13 mm. The 3 mm dosage has shown a slight degree of water loss (likely through evaporation) while the other two remain at a constant water volume. Day 7 (left), Day 9 (right).

Raw Biochar with BioMAG Floatability

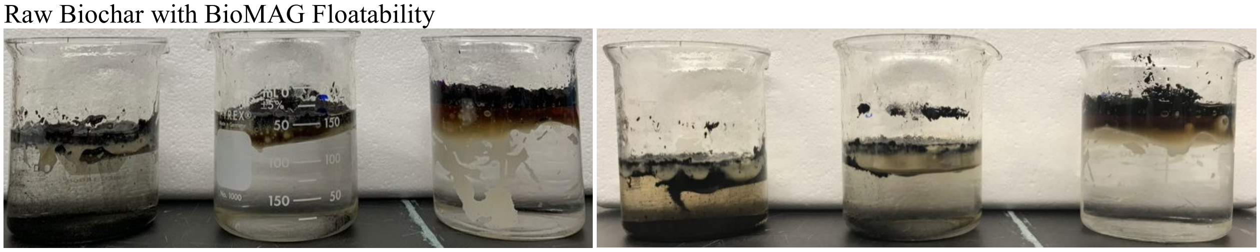

Figure 9. BioMAG (1.5 mm, 3 mm, and 6.5 mm) was applied and spread over the water surface with an equal dose of biochar applied on top (n = 3 replicates, the picture represents one example) (Day 1, left). Total (BioMAG + biochar) dosage per beaker from left to right: 3 mm, 6 mm, and 13 mm. The biochar in the 3 mm treatment has visibly fallen through the BioMAG layer and sunk to the bottom (Day 3, right). Significant water incorporation into biochar and evaporation occurred by Day 3 (right) for 3 and 6 mm treatments. The biochar has begun to integrate with the BioMAG by Day 3 in the 6 mm and the 13 mm treatments.

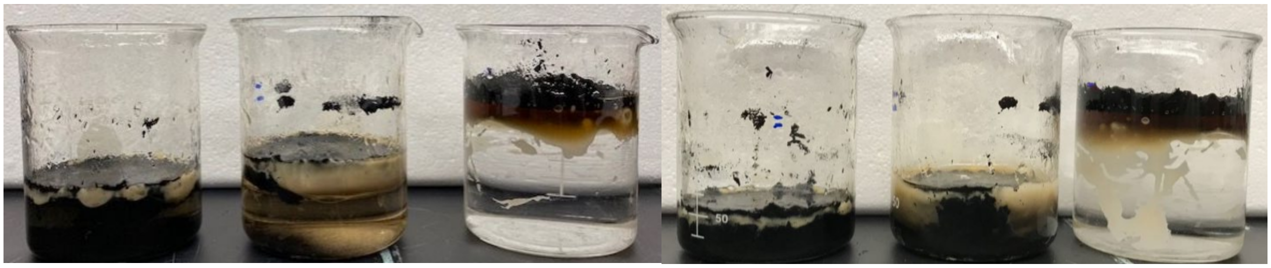

Figure 10. BioMAG (1.5 mm, 3 mm, and 6.5 mm) was applied and spread over the water surface with an equal dose of biochar applied on top (n = 3 replicates, the picture represents one example) (Day 7, left). Total (BioMAG + biochar) dosage per beaker from left to right: 3 mm, 6 mm, and 13 mm. The 3 mm treatment has incorporated/evaporated most of its water, and the BioMAG and biochar appeared to be mixed. The 6 mm beaker has retained some of its water content but has a more extensive mixing with the BioMAG to form a single layer. In the 13 mm treatment, the total volume of water has stayed nearly the same, and biochar has begun integrating with the BioMAG. Day 9 (right).

Top Views

a. Biochar

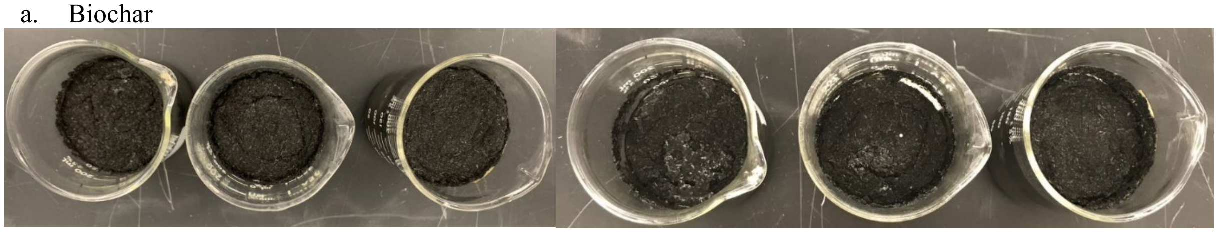

Figure 11. Biochar (100%) surficially applied to water (n = 3 replicates, the picture represents one example) (Day 1, left). Dosage per beaker from left to right: 3 mm, 6 mm, and 13 mm. Most of the biochar floats with a small fraction sunk and suspended. Significant water incorporation into biochar and evaporation occurred by Day 3 (right).

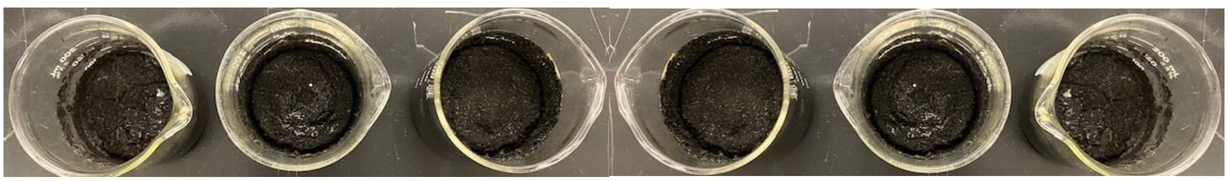

Figure 12. Biochar (100%) surficially applied to water (n = 3 replicates, the picture represents one example) (Day 7). Dosage per beaker from left to right: 3 mm, 6 mm, and 13 mm. Significant water incorporation into biochar and evaporation continued to occur. The 3 mm and 6mm treatments have lost almost all their water and have begun to settle completely by Day 9. The 13 mm treatment displays a slower rate of water incorporation/evaporation but has still mostly sunk by Day 9 (right).

b. BioMAG

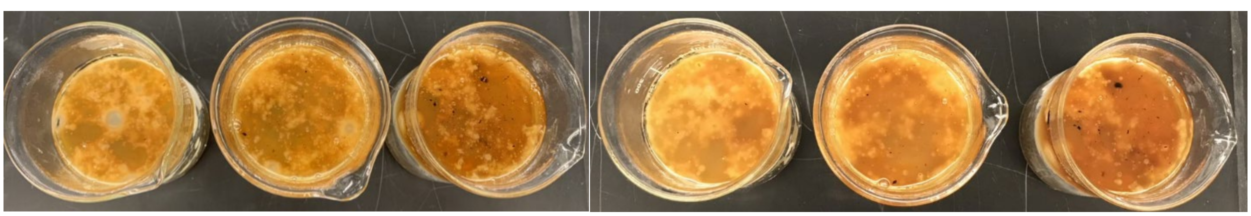

Figure 13. BioMAG is applied and spread over the water surface (n = 3 replicates, the picture represents one example). Dosage per beaker from left to right: 3 mm, 6 mm, and 13 mm. A thin darker layer formed on the top of the BioMAG by Day 3. This darker layer appeared to be is unexposed to water beneath it. Day 1 (left), Day 3 (right).

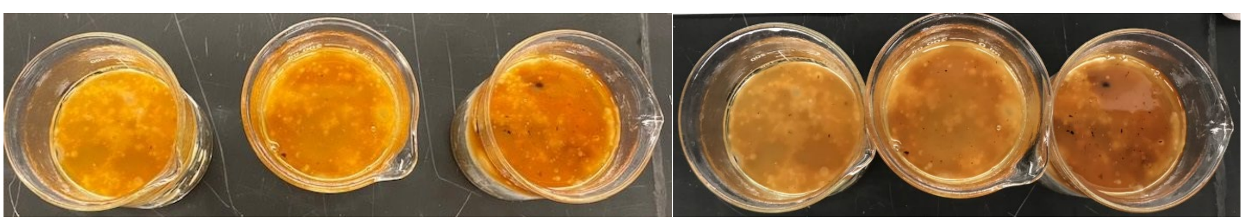

Figure 14. BioMAG applied and spread over the water surface (n = 3 replicates, the picture represents one example). Dosage per beaker from left to right: 3 mm, 6 mm, and 13 mm. The 3 mm dosage has shown a slight degree of water loss (likely through evaporation) while the other two remain at a constant water volume. Day 7 (left), Day 9 (right).

c. Biochar with BioMAG

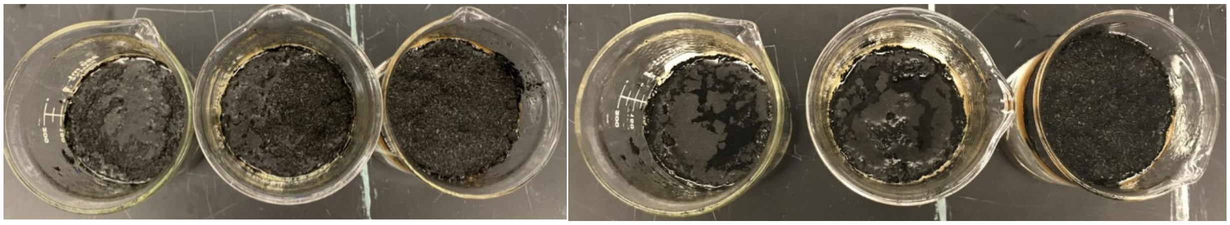

Figure 15. BioMAG (1.5 mm, 3 mm, and 6.5 mm) was applied and spread over the water surface with an equal dose of biochar applied on top (n = 3 replicates, the picture represents one example) (Day 1, left). Total (BioMAG + biochar) dosage per beaker from left to right: 3 mm, 6 mm, and 13 mm. The biochar in the 3 mm treatment has visibly fallen through the BioMAG layer and sunk to the bottom (Day 3, right). Significant water incorporation into biochar and evaporation occurred by Day 3 (right) for 3 and 6 mm treatments. The biochar has begun to integrate with the BioMAG by Day 3 in the 6 mm and the 13 mm treatments.

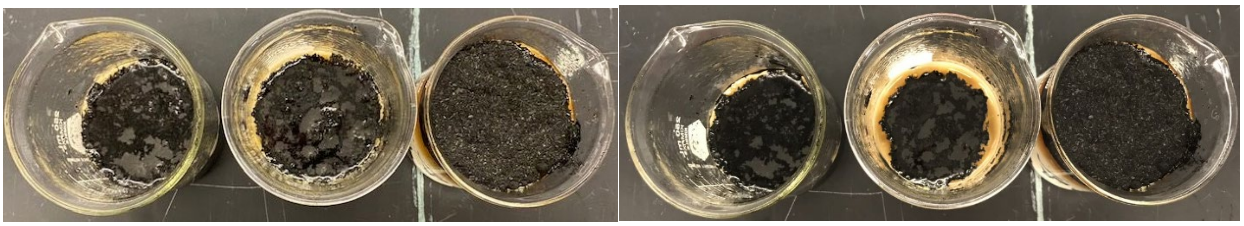

Figure 16. BioMAG (1.5 mm, 3 mm, and 6.5 mm) was applied and spread over the water surface with an equal dose of biochar applied on top (n = 3 replicates, the picture represents one example) (Day 7, left). Total (BioMAG + biochar) dosage per beaker from left to right: 3 mm, 6 mm, and 13 mm. The 3 mm treatment has incorporated/evaporated most of its water, and the BioMAG and biochar appeared to be mixed. The 6 mm beaker has retained some of its water content but has a larger mixed with the BioMAG to form a single layer. In the 13 mm treatment, the total volume of water has stayed nearly the same and biochar has begun integrating with the BioMAG. Day 9 (right).

Experiments 2 and 3: Testing Pelletized Biochar Floatibility: Effects of Binders

Side Views

a. BioMAG vs. BioMAG/water-based pellets. Treatment # ordered from left to right.
   i. Treatment 1 Pellet Composition: 70% biochar, 30% BioMAG
   ii. Treatment 2 Pellet Composition: 70% biochar, 15% BioMAG, 15% water
   iii. Treatment 3 Pellet Composition: 80% biochar, 20% BioMAG
   iv. Treatment 4 Pellet Composition: 80% biochar, 10% BioMAG, 10% water
   v. Treatment 5 Pellet Composition: 60% biochar, 40% BioMAG
   vi. Treatment 6 Pellet Composition: 60% biochar, 20% BioMAG, 20% water

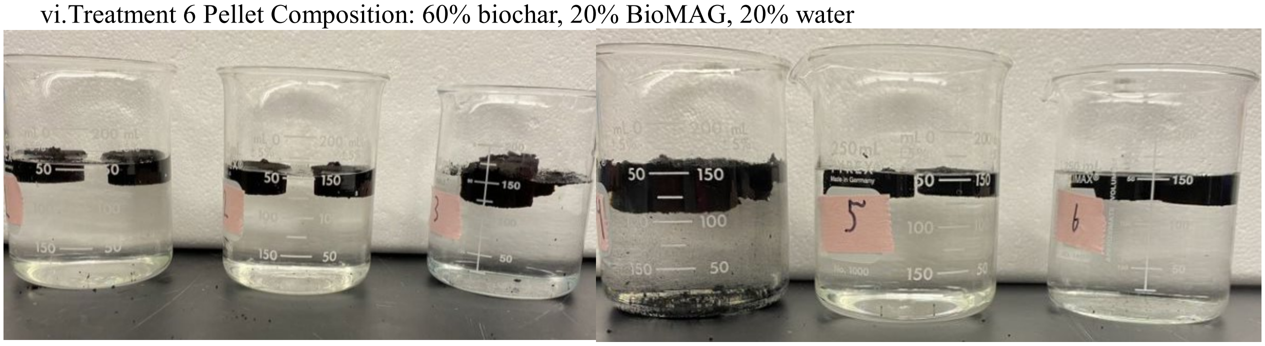

Figure 17. Day 1, pelletized biochar (using BioMAG and water as a binder) floating on water. All the pellets floated with Treatments 3 and 4, showing some signs of pellets breaking down.

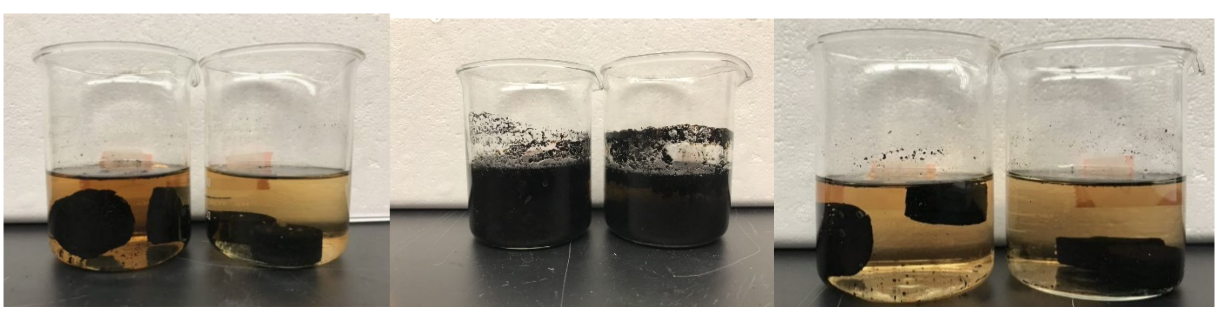

Figure 18. Day 3, pelletized biochar (using BioMAG and water as a binder) floating on water. Treatment # ordered from left to right. BioMAG started to dissolve out of the pellet and caused the water color change for all Treatments. All pellets have sunk except for one pellet in Treatment 5. Treatment 3 and 4 pellets have broken down completely.

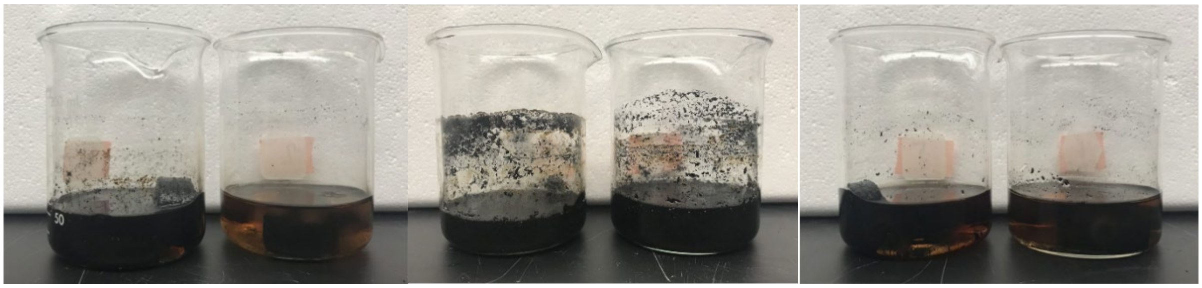

Figure 19. Day 9, pelletized biochar (using BioMAG and water as a binder) floating on water. Water was incorporated or evaporated. Solid pellets are still visible in Treatments 1, 2, 5, and 6. Pellets in Treatment 3 and 4 have dissolved.

b. Water vs. water/wax-based pellets. Treatment # ordered from left to right.

i. Treatment 1 Pellet Composition: 60% biochar, 40% water

ii. Treatment 2 Pellet Composition: 60% biochar, 20% water, 20% wax

iii. Treatment 3 Pellet Composition: 70% biochar, 30% water

iv. Treatment 4 Pellet Composition: 70% biochar, 15% water, 15% wax

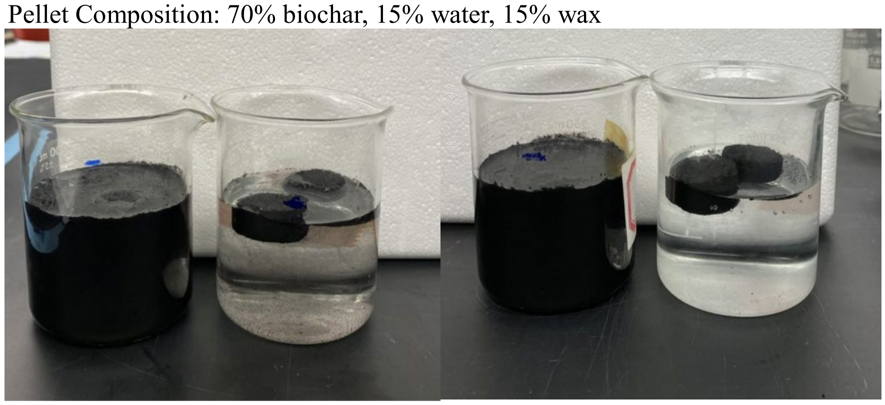

Figure 20. Day 1, pelletized biochar with water and wax. Treatment # ordered from left to right. Treatments 1 and 3 (biochar and water only) dissolved immediately, while Treatments 2 and 4 (biochar with water and wax) are still floating.

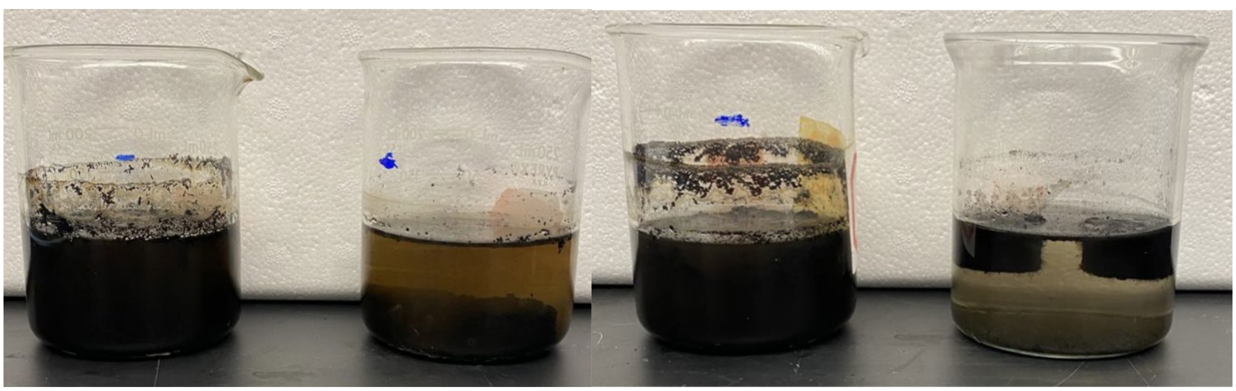

Figure 21. Day 9, pelletized biochar with water and wax. Treatment # ordered from left to right. Treatments 1 and 3 (biochar and water only) are dissolved. Treatment 2 (60% biochar, 20% water, 20% wax) has relatively intact pellets that have sunk. Treatment 4 (70% biochar, 15% water, 15% wax) had two nearly intact pellets floating.

Table 2. Summary of results of testing the floatability of biochar pellets.

Tested Combinations:	Duration of floating			
	Day 1	Day 3	Day 7	Day 9
Experiment 1: Biochar powder vs. BioMAG vs. Layered Biochar powder and BioMAG				
Raw Biochar: 3 mm	Y[a]	Y	N[b]	N
Raw Biochar: 6 mm	Y	Y	Y	N
Raw Biochar: 13 mm	Y	Y	Y	N
Raw BioMAG: 3 mm	Y	Y	Y	Y
Raw BioMAG: 6 mm	Y	Y	Y	Y
Raw BioMAG: 13 mm	Y	Y	Y	Y
Layered BioMAG and Biochar: 3 mm	Y	Y	Y	N
Layered BioMAG and Biochar: 6 mm	Y	Y	Y	Y
Layered BioMAG and Biochar: 13 mm (6.5 mm + 6.5 mm)	Y	Y	Y	Y
Experiment 2: BioMAG vs. BioMAG/water-based pellets				

Pellet Composition: 70% biochar, 30% BioMAG	Y N -[c] N
Pellet Composition: 70% biochar, 15% BioMAG, 15% water	Y N - N
Pellet Composition: 80% biochar, 20% BioMAG	Y N - N
Pellet Composition: 80% biochar, 10% BioMAG, 10% water	Y Y - N
Pellet Composition: 60% biochar, 40% BioMAG	Y Y - N
Pellet Composition: 60% biochar, 20% BioMAG, 20% water	Y N - N
Experiment 3: Water vs. water/wax-based pellets	
Pellet Composition: 60% biochar, 40% water	N - - N
Pellet Composition: 60% biochar, 20% water, 20% wax	Y - - N
Pellet Composition: 70% biochar, 30% water	N - - N
Pellet Composition: 70% biochar, 15% water, 15% wax	Y - - Y

[a] "Y" represents that the pellet was floating at that time.
[b] "N" represents that the pellet was not floating at that time.
[c] "-" represents no data collected for that specific day.

Discussion

Preliminary observations confirmed the potential for improving biochar floatability in both powder (raw) and pelletized forms. A layer of soybean-based epoxy can support raw biochar powder. The best treatment was the layered BioMAG (6.5 mm) with 6.5 mm of biochar on top. Also, biochar powder can be held together with combinations of binders and made into pellets with have more practical application potential. The best pellet treatment was composed of 70% biochar, 15% water, and 15% wax.

Our preliminary observations warrant further research to address:

1. What is the rate of incorporation of liquid into biochar, and how does it affect evaporation? This could be achieved with the periodic weighing of each treatment.
2. How does the floatability in water compare with the floatability in manure?
3. How does the biochar and biochar pellets floatability affect the ability to mitigate gaseous emissions from manure?
4. How do the specific properties of biochar impact its ability to integrate with binders effectively?
5. What are the techno-economic constraints and barriers for adopting biochar as preferred treatment of gaseous emissions from stored manure?

Conclusions

The objective was to determine raw biochar, soybean-derived epoxy (BioMAG), and biochar pellets' (made with a combination of water, wax, and BioMAG) ability to float in water. Preliminary observations confirmed the potential for improving biochar floatability in both powder (raw) and pelletized forms. A layer of soybean-based epoxy can support raw biochar powder. The best treatment was the layered BioMAG (6.5 mm) with 6.5 mm of biochar on top for at least 9 days. Also, biochar powder was held together with combinations of binders and made into pellets with have more practical application potential. The best pellet treatment was composed of 70% biochar, 15% water, and 15% wax. This mix of biochar and binders stayed afloat for at least 9 days. Both successful results warrant further research and trials of the best treatments on manure to mitigate gaseous emissions.

Acknowledgments

We are thankful to the Iowa State University Honors Program for co-funding students' research (Cameron Cimino, Cail Donkersloot, Ryan Ungs) on this project. 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.

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