Biochar from Corn Waste as Biofilter in a Recirculating Aquaculture System

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Abstract: The use of biofilter with the application of biochar technology for the improvement of water in a recirculating aquaculture system (RAS) provides a lot of advantages in aquaculture production. The research aimed to devise a biofilter system for the enhancement of TAN and un-ionized ammonia levels in a RAS using biochar from corn cobs for Nile tilapia Oreochromis niloticus production. It has five main parts: fish tank, biochar filtration tank, sediment filter, sludge filter and pump. The fish tank used is a 1 m³ plastic cubical tank. The biochar filtration tank with a height of 85 cm and a diameter of 30 cm. The sludge filter has a height of 52 cm with a diameter of 13 cm. An electric water pump was used to recirculate the water. The system was fabricated and were able to effectively enhance the level of total ammonia nitrogen (TAN) at a rate of 0.56 ppm per hour for every 1kg biochar and 0.72 ppm per hour for the reduction of un-ionized ammonia. The devised biofilter proved to reduce the level of TAN by 9.45 ppm and un-ionized ammonia levels by 2.18 ppm in 6 hours and 30 minutes using corn cob biochar.

Keywords: Biochar, Biofilter, Recirculating Aquaculture Systems (RAS), Total Ammonia Nitrogen (TAN), Un-ionized ammonia

I. INTRODUCTION

Research and studies about biochar technology are vastly growing over the years because of its multidisciplinary approach and different applications. Biochar is a carbon-rich solid material produced by thermal decomposition of organic material or biomass in the absence or under limited supply of oxygen (Lehman and Joseph, 2009).

Ammonia and nitrite are toxic to fish. Ammonia in water occurs in two forms: ionized ammonium (NH₄⁺) and un-ionized ammonia (NH₃). The latter, NH₃, is highly toxic to fish in small concentrations and should be kept at levels below 0.05 mg/L. The total amount of NH₃ and NH₄⁺ remains in proportion to one another for a given temperature and pH, and a decrease in one form will be compensated by conversion of the other. The amount of un-ionized ammonia in the water is directly proportional to the temperature and pH. As the temperature and pH increase, the amount of NH₃ relative to NH₄⁺ also increases. The ammonia poisoning of fish is as imminent danger in a RAS (Helfrich and Libey, 2019). With this, a biofiltration system plays a vital role in maintaining a good aquaculture water quality.

Recirculating Aquaculture Systems (RAS) has been in existence, in one form or another, since the mid-1950s. However, only in the past few years has its potential to grow fish on a commercial scale been realized. New water quality technology, testing and monitoring instrumentation, and computer enhanced system design programs, much of it developed for the wastewater treatment industry, have been incorporated and have revolutionized our ability to grow fish in tank culture. Nevertheless, despite its apparent potential, RAS should be considered a high-risk, experimental form of agriculture at this time. It can be used to culture high densities of fish annually, but its ability to do so economically remains to be demonstrated, conclusively and repeatedly (Helfrich and Libey, 2019).

With these characteristics, a potential to develop biochar from corn cobs for improving TAN and un-ionized ammonia levels in a RAS shows a potential researchable area since corn cobs are abundant in supply, low-cost, and readily available in the area. With the expansion of tilapia culture, together with the shortage of freshwater and competition of the water use into different applications, and with the growing number of human populations through the years, tilapia farming has been shifted from traditional semi-intensive systems to more intensive production systems such as the production in fish tanks and fish cages with the use of a RAS.

RAS is characterized by its ability to support extremely high stocking densities and high net production with a limited volume of water requirements. However, high stocking density will result in high fish wastes which are toxic ammonia compounds in the form of TAN and un-ionized ammonia excreted into the water and uneaten feed particles that need to be removed.

Biochar has the potential role in improving aquaculture water quality in fish culture by lowering the level of TAN and un-ionized ammonia in a RAS.
Also corn cobs has a potential media in improving aquaculture water. The use of charcoal for water purification to remove unwanted dissolved organic pollutants is well established. However, there has been limited research on the potential of biochar to improve the quality of aquaculture water in RAS for fish production. Therefore, the project will contribute to the aquaculture sector by establishing the potential of biochar filtration in improving the quality of aquaculture water specifically in reducing the TAN concentration.

II. MATERIALS AND METHODS

A. Preparation and Carbonization of Corn Cobs

Corn cobs samples were collected. Impurities and other foreign materials were removed to attain the uniformity of the samples. A pyrolytic converter was used to carbonize the corn cobs. For each batch of the biomass samples, ten kilograms (10 kg) of samples were loaded inside the kiln. Rice hulls were fed around the fuel feeder every 20 min and when the fire reached the top feeder until the samples were fully carbonized. The biomass samples were subjected to heat with minimum presence of oxygen at an average of five hours. Carbonized samples were left inside the kiln overnight to release the heat inside the kiln and to make sure that it would not become ash when in contact with air. After carbonization, samples were crushed to achieve uniformity then sieved manually within wire mesh sizes of 1 and 5 mm to attain a 1-5 mm biochar sample size. Figure 1 shows biochar production and utilization method.

B. Devising a Biochar Filtration System in RAS

A biochar filtration system for the reduction of TAN and un-ionized ammonia, removal of the feed residues, and aeration in grow out tank was devised. The system was devised from the principle of operation of a commercial water filtration system (Figure 2). The first stage of the system aimed to remove the feed residues by suctioning the bottom layer of the tank using a water pump. After the residues were filtered, the water was then transported to the biochar container wherein the TAN was adsorbed and reduced. To avoid the black coloring of the water in the biochar container, another filter system was installed. Lastly, the filtered water was released back to the fish tanks. The flow of water into the tank was then used as aeration in the fish tanks during the biochar filtration process. With this, there was no need for an aerator to provide for the desired dissolved oxygen level during the operation of the biochar filtration system.
C. Un-ionized Ammonia Adsorption Capacity of Biochar
Un-ionized ammonia (NH$_3$) which was more toxic to fish than ionized ammonia (NH$_4^+$) was calculated from total ammonia readings (Emerson et al., 1975). Total ammonia is the sum of ammonia (NH$_3$) and ammonium (NH$_4^+$) concentrations. A multi-parameter tester was used to determine the adsorption capacity of biochar in terms of the total ammonia.

D. Amount of TAN Adsorbed and Removal Efficiency using Biochar
The amount of TAN adsorbed and removal efficiency of using biochar was computed using Equation 1.

$$ q_e = V/W \times (C_f - C_i) $$

where:
- $q_e$ - the amount of TAN and un-ionized ammonia removed (mg·g$^{-1}$)
- $C_f$ - final TAN concentration, (mg·L$^{-1}$)
- $C_i$ - initial TAN concentration, (mg·L$^{-1}$)
- $V$ - volume of the aquaculture water in tank, L
- $W$ - weight of the biochar, g

Two basic approaches were used in interpreting the experimental results for adsorptive capacity. Nameni et al (2008) computed the percent of MB adsorbed (adsorption efficiency, %) using the formula in Equation 2.

$$ \% \ TAN \ adsorbed = \left( \frac{C_i - C_f}{C_i} \right) \times 100 $$

where:
- $C_i$ - initial concentration,
- $C_f$ - final concentration

E. Statistical Analysis
Paired t-test was performed for the validation of the results in an actual RAS using the devised biochar filtration systems. Comparison among treatment means was analyzed using Duncan Multiple Range Test (DMRT) at 5% level of significance.
III. RESULTS AND DISCUSSION

A. Corn Cob Properties
Corn cobs properties were determined by performing proximate analysis. Properties such as percent moisture, volatile combustible matter, ash and carbon content were determined to assess its quality. The higher the fixed carbon from biomass, the higher the biochar yield.

Proximate analysis revealed that the percent moisture of the corn cobs samples was 4.43 percent. Results revealed that the amount of water in biochar is within the acceptable value and much lower than the accepted moisture content of 10%. The moisture content has no effect on the adsorptive property of the biochar. Hence, if the moisture content is high, the more susceptible is the carbon to fungi growth, thus, the shelf life is reduced.

The carbon, oxygen and hydrogen component of corn cobs also known as the volatile combustible matter revealed a 14%. The result of the volatile matter is considered excellent which means that the carbonization is prolonged and at a high temperature. This also signifies that the corn cobs used is of good quality. The ash content of the biochar samples revealed that corn cob has only 6.65% which was within the acceptable values. The desirable value of ash content of activated carbon ranges from 1-20 % as mentioned by Abdul (2007). Ash content dictates the quality of an activated carbon since it reduces its mechanical strength. Corn cob has fixed carbon content of 80.3%.

The amount of TAN adsorbed and removal efficiency using biochar was attributed to thermolysis of cellulose. This cellulose or lignin is considered as the main component of biochar which formed carboxyl groups. This functional groups were the basis for the effective adsorption of ammonia (Asada, et.al. 2002).

B. Biochar Filtration in a Recirculating Aquaculture Systems
The devised biochar filtration system in RAS (Figure 3) aimed to enhance the TAN and un-ionized ammonia level in RAS. It also served as a device to take in the sludge and sediment particles from grow out tank; filter the accumulated sludge, solid particles, and sediments; and for additional aeration inside the tank during the biochar filtration process.

The biochar filtration system was composed of five main parts, namely: fish tank, pump, biochar filtration tank, sediment filter, sludge filter and pump. The fish tank used for Nile tilapia production was a 1 m$^3$ plastic cubical tank. The biochar filtration tank with a height of 85 cm and a diameter of 30 cm was filled with 5-9 mm gravel at the bottom, 1 kg of 5-10 mm corn cob above the gravel, and then followed by 1-5 mm of sand on top of the corn cob (Figure 4).

Fig 3. The devised biochar filtration system
The sediment filter aims to filter the sediments as well as the black coloring of the water when mixed with biochar (Figure 5). The sludge filter was used to filter the accumulated sludge and other solid particles inside the tank such as unconsumed feeds and fish excreta that settled at the bottom part of the tank (Figure 6). A sweeper/suction pipe was connected to the filter to suck the sludge particles below the experimental tank. Also, this served as a first stage filtration so that the sludge particles were not transported to the biochar container. The sludge filter has a height of 52 cm with an inside diameter of 12 cm and an outside diameter of 13 cm.

An electric water pump was used to circulate the aquaculture water from the experimental tank, passing it through the sludge/solid filter, to the biochar filtration tank, to the sediment filter tank and lastly, to transport back the water to the experimental tank;
C. Operation of a Biochar Filtration System
The biochar filtration system was operated by pumping the water from the RAS tank passing to the sludge filter then filled up to the biochar container wherein biochar filtration takes place. The aquaculture water was then pass through to the sediment filter then flows back to the RAS tank (Figure 7).

D. Performance of the Devised Biochar Filtration System in a RAS
The performance of the devised biochar filtration system was evaluated through actual validation of the TAN and un-ionized ammonia reduction in an actual fish production environment (fish tank) in a RAS and was compared to the fish tank without biochar filtration.

E. TAN Reduction using the Biochar Filtration System
Results of the TAN reduction using the biochar filtration system revealed that for eight hours of operating the biochar filtration system, there is an evident enhancement of TAN in the grow-out tank. First run showed a decrease of 4.48 ppm from 6.12 ppm to 1.64 ppm. Another run showed a 4.47 ppm decrease from 5.8 to 1.33 ppm and lastly, a decrease of 3.35 ppm from the initial reading of 4.97 to 1.43 ppm (Figure 8).
F. Un-ionized Ammonia Reduction using Biochar Filtration System

Un-ionized ammonia reduction using biochar filtration system was calculated from total ammonia readings (Emerson, et al., 1975). Data showed that the average un-ionized ammonia levels were above the desirable level (Figure 11). The ideal un-ionized ammonia level for fish production was 0.01 ppm.

![Graph showing un-ionized ammonia reduction using biochar filtration system](image)

Fig. 9. Un-ionized ammonia reduction using the biochar filtration system

G. TAN Reduction at Different Stages of Biochar Filtration

The amount of TAN reduced at different filter stages was measured and evaluated. Results revealed that RAS tank had the lowest TAN reduction of 3.45 ppm after seven-hours of observation at a rate of 0.49 ppm per hour.

| Time of observation (hr) | RAS Tank (ppm) | Filter 1 (Sludge Filter) (ppm) | Filter 2 (Biochar Filter) (ppm) | Filter 3 (Sediment Filter) (ppm) |
|-------------------------|----------------|-------------------------------|-------------------------------|---------------------------------|
| 0.0                     | 4.97           | 5.20                          | 5.35                          | 5.17                            |
| 0.5                     | 5.03           | 4.80                          | 3.09                          | 3.72                            |
| 1.0                     | 4.73           | 4.56                          | 3.94                          | 3.93                            |
| 1.5                     | 4.26           | 4.19                          | 3.77                          | 3.78                            |
| 2.0                     | 4.01           | 3.97                          | 2.80                          | 3.01                            |
| 2.5                     | 3.55           | 3.22                          | 2.08                          | 2.23                            |
| 3.0                     | 2.87           | 2.66                          | 1.90                          | 1.86                            |
| 3.5                     | 2.43           | 2.33                          | 1.71                          | 1.65                            |
| 4.0                     | 2.09           | 1.98                          | 1.53                          | 1.57                            |
| 4.5                     | 2.01           | 1.92                          | 1.23                          | 1.42                            |
| 5.0                     | 1.86           | 1.70                          | 1.15                          | 1.11                            |
| 5.5                     | 1.67           | 1.75                          | 1.09                          | 1.03                            |
| 6.0                     | 1.73           | 1.64                          | 1.26                          | 1.15                            |
| 6.5                     | 1.55           | 1.71                          | 1.05                          | 1.08                            |
| 7.0                     | 1.52           | 1.43                          | 1.12                          | 1.10                            |

Table 1. TAN reduction at different stages of biochar filtration

Biochar filtration (biochar filter) tank had the highest TAN reduction of 4.23 ppm with a rate of 0.60 ppm per hour, followed by the sediment filter of 4.07 ppm at a rate of 0.58 ppm per hour. Next was the sludge filter with 3.77 ppm at a rate 0.54 ppm per hour (Table 2). Results revealed that at the first filter (sludge), there was no significant difference on the reduction of TAN after passing through it while there was a significant difference on the second filter (biochar filter) before and after the biochar filtration. On the last filter, (sediment filter) results showed that there was no significant difference before and after passing.
Results indicated that biofilter using corn cobs has a potential for the enhancement of TAN and un-ionized ammonia levels in RAS. It can be concluded that the percent moisture of the corn cobs samples was 4.43 percent, volatile combustible matter of 14%, ash content of 6.65% and fixed carbon content of 80.3%. The biochar filtration system successfully reduced the level of TAN at a rate of 0.56 ppm per hour for every 1kg biochar and 0.72 ppm per hour for the reduction of un-ionized ammonia in a 1 cubic meter fish tank under RAS. These results indicated that unutilized corn cobs in a biofilter can be used to mitigate the negative effect of un-ionized ammonia in a RAS.

V. ACKNOWLEDGMENT

It is with immense gratitude and deepest appreciation that the author expresses warmest gratitude and heartfelt appreciation to the Institutions and people who contributed to the completion of this project:
Tarlac Agricultural University for funding the project.
Department of Agricultural and Biosystems Engineering, College of Engineering, Central Luzon State University for the instruments and other materials used in the project. Department of Science and Technology – Engineering Research and Development for Technology (DOST-ERDT).
Bennidict, ZheyAnne and Zhia Kate, who served as inspiration in finishing this project; and, above all, to our Almighty God for all His endless blessings.

LITERATURE CITED

[1] Asada, T., Ishinara, S., Yamane, T., Toba, A., Yamada, A., and Oikawa, K. 2002. Science of Bamboo Charcoal: Study on Carbonizing Temperature of Bamboo Charcoal and Removal Capability of Harmful Gases. Journal of Health Science, 48(6) 473-479.
[2] Berger, C. 2012. Biochar and activated carbon filters for greywater treatment-comparison of organic matter and nutrients removal. Master Thesis, Swedish University of Agricultural Sciences, Uppsala, Sweden. 45 pp.
[3] Dubey, S.P., K. Gopal, and J.L. Bersillon. 2009. Utility of Adsorbents in the Purification of Drinking water: A Review of Characterization, Efficiency and Safety Evaluation of Various Adsorbents. Journal of Environmental Biology 30:327-332.
[4] Ebeling, J. 2020. Biofiltration-Nitrification Design Overview. https://cals.arizona.edu/azuqsa/ista/ISTA7/RecircWorkshop/Workshop%20PP%20%20&%20Misc%20Papers%20Adobe%202006/7%20Biofiltration/Nitrification-Biofiltration-Nitrification%20Design%20Overview.pdf. Cited 20 January 2020.
[5] Ekubo, A.A., and J.F.N. Abowei, 2011. Review of Some Water Quality Management Principles in Culture Fisheries, Research Journal of Applied Sciences, Engineering and Technology, 3(2), pp 1342-1357.
[6] Helfrich, A., Libey, G. 2019. Fish Farming in Recirculating Aquaculture Systems. http://fisheries.tamu.edu/files/2013/09/Fish-Farming-in-Recirculating-Aquaculture-Systems-RAS.pdf. Cited 14 January 2020.
[7] Lehmann, J. and Joseph, S. 2009. Biochar for Environmental Management: Science and Technology. pp. 289-296. 22883 Quicksilver Drive, Sterling,VA 20166-2012, USA.
[8] Lehmann J., 2007. A handful of carbon. Nature 447:143–144. https://doi.org/10.1038/447143a. Cited January 15, 2020.
[9] Lehmann J., and Joseph S., 2015. Biochar for Environmental Management: Science, Technology and Implementation. 2nd edition. Routledge, London, pp 1–1214.
[10] Lennard, J., 1932. Processes of adsorption and diffusion on solid surfaces', Transactions of the Faraday Society. Volume 28, 1932. pp. 333-359.
[11] Sichula, J., Makasa, M., Nkonde, G., Kefi, S., & Katongco, C., 2011. Removal of Ammonia from Aquaculture Water Using Activated Carbon. ISSN: 1997-0455
