博 士 論 文 の 要 約

博士の専攻分野の名称：　博　士（農学）　　　氏名: Md. Mahmudul ISLAM

Synthesis of biochar-based slow-release fertilizer from nutrient-rich organic waste

(栄養豊富な有機性廃棄物を原料とした緩効性バイオ炭肥料の合成)

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Introduction

The two biggest challenges of the twenty-first century are to mitigate the effects of climate change and sustainably increase food production for the growing population. The single action of increasing organic matter content in agricultural soils can help to mitigate both challenges (Machmuller et al., 2015). Ensuring increased carbon sequestration in agricultural soils by higher organic matter input could offset the carbon emission from this sector. Additionally, increasing organic matter in agricultural soils has a proven record of enhancing soil quality and restoring soil health. Healthy soil can in turn support sustainable and nutritious food production. Therefore, for a sustainable future, soils should be kept productive with increased organic matter input that might mitigate climate change and food insecurity.

The application of organic matter directly to soil has been criticized for its short residence time, and potential negative effects like rapid GHG emission, pathogen introduction, etc. Thus, with long-term stability in soil and carbon sequestering potential, biochar (thermochemically treated organic matter in low oxygen conditions) could become a safe method of organic waste circulation with sustained agronomic benefits. Those benefits include but are not limited to improved soil pH, CEC, water retention, hydraulic conductivity, bulk density, nutrient retention, etc. (El-Naggar et al., 2019).

Despite the numerous benefits of biochar, it has not been extensively adopted by farmers yet. The most prominent reason behind this is the high cost, energy-intensive production, and sophisticated technology needed for biochar production (Cha et al., 2016). However, significant additional benefits of biochar will encourage farmers to extensively utilize it in the field. Nutrient-rich biochar could be a reasonable solution in this regard through substituting the use of expensive chemical fertilizers (Prakongkep et al., 2015). If biochar were able to supply essential plant nutrients for crop production, it would have served as a tool for both carbon sequestration and soil fertilization. Therefore, the overall objective of this study is to determine whether biochars produced from nutrient-rich feedstocks can release sufficient nutrients for plant growth and become an alternative to chemical fertilizers. In this way, this study aims to establish a biochar-based sustainable nutrient circulation system that can simultaneously mitigate climate change, support sustainable food production and decrease the pressure on synthetic chemical fertilizers.

This Ph.D. dissertation is consisting of three individual research projects (Chapters 2, 3, and 4). A brief description of the projects is presented below.

Project 1. Release of essential plant nutrients from manure- and wood-based biochars

Many previous studies denied biochars' nutrient-supplying potential, mainly because of utilizing nutrient-poor feedstocks (Hussain et al., 2017). Even, some nutrient-rich biochars have nutrient elements as crystalline minerals and show very little solubility (Ca, P), which is completely different than fast-releasing conventional chemical fertilizers (Prakongkep et al., 2015). Then again, N contained in biowastes has the tendency to become volatile (syngas) during biochar production, and only 25–35% is conserved in char materials. Some biochars have been also reported to absorb essential plant nutrients (N, Ca) from the soil solution, making those unavailable for plant uptake followed by reduced crop yield (Limwikran et al., 2018). Thus, most increases in crop yield by biochar application are not due to significant nutrient release, but rather improved physicochemical properties of soil (Joseph et al., 2021). On the other hand, few studies have reported biochar's ability to supply essential plant nutrients (Hossain et al., 2020), however, the nutrient release potential of biochar is still not well understood. The release of nutrients from biochar often depends on feedstock, pyrolysis temperature, and application amount (Ippolito et al., 2020). Therefore, the identification of appropriate feedstock and production temperature to produce biochar that can supply sufficient phytoavailable nutrients to the soil is essential. This first project intended to utilize nutrient-rich feedstocks to produce biochar-based fertilizer and investigate their potential mechanism to be a climate-smart alternative to conventional chemical fertilizers. In the research project, we hypothesized that greater N content and the presence of coexisting nutrient ions in manure-based biochars will enhance net N mineralization. It was further hypothesized that enhanced N mineralization will increase the P and K availability in soil

Materials and methods: Two separate incubation experiments were conducted to determine the nutrient release potential of different biochars and to reveal the mechanism of the release. Biochars were produced from nutrient-rich chicken (CMB) and dairy manure (DMB), and nutrient-poor Japanese larch (JLB) at 300 and 500 ℃ in a muffle furnace for 1 hour. NPK release in incubated clay loam soil (in glass containers, for 120 days at 20℃) from biochars was compared to the recommended fertilizer dose of sweet corn. The biochars were applied at a rate of 2% dry basis. After definite time intervals, soils were extracted with suitable extractants and available NPK was determined either by capillary electrophoresis or ICP-MS, following the standard procedure. Another incubation experiment was conducted simultaneously to easily separate biochars from the soil. Nylon meshes were used to sandwich biochars in two equal layers of soil. The nylon meshes could facilitate the interaction of soil and biochar by allowing the passage of water, air, and microbes. After 120 days of interaction, incubated biochars were recovered from nylon mesh and subjected to several tests. Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), BET-specific surface area analysis, cation exchange capacity (CEC), etc. were used to determine the changes in biochar before and after incubation in soil (Piash et al., 2021).

Results and discussion: The findings showed that CMBs and DMBs produced at both 300 and 500 ℃ could supply adequate NPK and PK respectively, for optimum sweet corn production. Further analysis revealed that dissolution of amides ($-CONH_2$) was the main mechanism to work behind substantial N release from CMB biochars. Initially, the CMB produced at 300 ℃ had about 10% nitrogen and it released the maximum amount of N. However, N content was significantly low in CM500, mostly due to the emission of nitrogenous gases stimulated by higher temperatures during the production process.

Therefore, N release from CM500 was also low, although was sufficient compared to the recommended chemical fertilizer dose. On the other hand, dissolution of ortho-phosphates, and sylvite (KCl) were the major mechanisms behind most PK releases. In general, a higher production temperature (500 °C) increased P and K content and release from manure biochars. The wood-derived JLB biochars were proved to be incapable of supplying any essential nutrients (NPK) for plant uptake, rather decreased nutrient availability in the soil in some cases. Results also indicated that the aging of biochar in soil had a positive effect on increasing cation exchange capacity (CEC). Besides, all the biochars have been seen to increase carbon content in soil after 120 days of incubation, regardless of the feedstock. Overall, this study has revealed the potential of manure-derived biochars for use as a comprehensive fertilizer or as a complementary amendment to the conventional chemical fertilizer while storing carbons in soil.

Project 2. Synthesizing biochar-based fertilizer with sustained phosphorus and potassium release: Co-pyrolysis of nutrient-rich chicken manure and Ca-bentonite

The release of nutrients from many organic fertilizers is relatively fast due to the huge amount of soluble nutrients and stimulated microbial decomposition. These fertilizers sometimes cause significant deterioration of the surrounding environment. Therefore, the development of slow-release organic fertilizer from nutrient-rich agricultural waste is essential to enhance NUE and reduce environmental impacts.

In our initial project, it was reported that chicken and dairy manure-based biochars (2% w/w) can effectively supply nutrients essential for optimum sweet corn production (Piash et al., 2021). In particular, chicken manure (CM) biochar produced at 300 °C proved to be a complete source of essential N, P, and K. It was further reported that the rapid dissolution of orthophosphates and KCl is the main mechanism of P and K release from biochar, but the fast release of P and K remains a major hurdle in generating biochar-based fertilizers (BBFs) with high NUE. Thus, controlling the release of P and K from high-nutrient CM biochar could be an innovative strategy to produce biochar-based slow-release fertilizer (BSRF) without the need to add chemical nourishments.

Several approaches have been proposed to date to slow down the nutrient release from BBF but most require expensive modification techniques such as metal modification, magnetic activation, or polymer coating (An et al., 2021; Shi et al., 2020) together with additional nutrient loading (by direct mixing, compounding, or absorbing from aqueous solutions). Recently, co-pyrolysis of naturally available bentonite with biomass was shown to form stronger bonds between carbon in the biochar and elemental nutrients, efficiently slowing their release (An et al., 2020; Shi et al., 2020). However, no previous study has suggested an appropriate bentonite type for BSRF production. The type of bentonite can have a significant effect on biochar physicochemical properties, and the application of inappropriate bentonite can adversely affect the soil. For example, Na-bentonite can stimulate salt stress in plants if applied together with salt-containing manure-based biochars generated from CM. In contrast, the addition of Ca-bentonite with organic material or fertilizer has been reported to increase soil water storage, macro-aggregates, and the above-ground biomass and grain yield of millet (Mi et al., 2017). Exchangeable Ca^{2+} in bentonite might also mitigate the negative effects of salt in BBF and become an effective adsorbent of ortho-phosphates (Markou et al., 2018).

In this study, we co-pyrolyzed Ca-bentonite with CM to test two hypotheses: that Ca-bentonite will (i) facilitate the formation of less soluble Ca-Ps, retarding P release; and (ii) adsorb soluble K^+ in its crystalline structure, slowing K release in soil.

Materials and methods: Initially, we mixed 10 or 25% Ca-bentonite (dry basis) with chicken manure and dried it in an oven at 105 °C. Then, the mixtures were pyrolyzed in a muffle furnace at 300 °C for one hour. The produced biochars with only CM, 10% Ca-bentonite, or 25% Ca-bentonite were designated as CMB, B10CMB, and B25CMB, respectively. The produced biochars were first subjected to be characterized by elemental analysis, FTIR, XRD, and SEM-EDS. Then, those biochars were used for incubation study to check whether the proposed technology can efficiently retard the P and K release. In the first project, it was revealed that some constituents (available Al, Ca, Si) of clay loam soil could significantly impact nutrient release from BBF (Piash et al., 2021) and thus here, less reactive quartz sand was included as a parallel medium, together with clay loam soil, to compare nutrient release and fixation. We compared the release of 2% biochar with recommended fertilizer dose of sweet corn for 90 days. After definite time intervals, soil and quartz samples were extracted and the available NPK was determined as described in the first project. After 90 days of incubation study, we statistically analyzed the nutrient release data for potential slow-release by co-pyrolysis of Ca-bentonite. Additionally, we also compared the microbial diversity (16s rRNA) in control and amended treatments after the incubation period, to determine if treatments can significantly affect the microbial composition (Piash et al., 2022).

Results and discussion: Fourier transform infrared spectroscopy (FTIR) and energy-dispersive X-ray spectroscopy showed that readily soluble ortho-Ps became less-soluble Ca/Mg-Ps by co-pyrolysis. This transformation of soluble P is expected to retard P release. The phosphorus release test showed that the addition of 25% Ca-bentonite before pyrolysis retarded P release in both the media (quartz and clay loam) but was not significant throughout the incubation period. The P-release reduction by Ca-bentonite was more prominent in alkaline quartz. In this medium, P-release was 97, 84, and 78%, respectively, from CMB, B10CMB, and B25CMB after 90 days of incubation, suggesting that B25CMB considerably retards the release of P. In addition, because of K adsorption in crystalline bentonite, 22% slower K release was observed in CMB with 25% Ca-bentonite (B25CMB) than the pristine CMB. Co-pyrolysis at 300 °C after mixing with Ca-bentonite is expected to decrease the basal space of bentonite, which might restrict the easy exchange of nutrients, specially K. The decrease in basal space due to co-pyrolysis should eliminate the need for coating and K would be released slowly depending on the ionic concentration of the soil. On average, P and K release from CMBs in coarse sand was respectively 38% and 24% higher whereas greater N release (49%) occurred in clay-loam soil. The results also indicated that >10% Ca-bentonite should be used to sufficiently retard P and K release from CMB. Microbial diversity analysis revealed that the addition of Ca-bentonite had no significant effect on the diversity of the identified microbes in soil and that diversity decreased slightly with the increasing amount of bentonite added. Even though Ca-bentonite-incorporated CMBs exhibited promising slow-release (P and K) performance, they had no impact on retarding N release. Therefore, further modification is required to produce a complete slow-releasing biochar-based fertilizer.

Project 3. Effective encapsulation of biochar-based fertilizer: Utilizing the grafting potential of chitosan for sustained nutrient release

Nitrogen is the most crucial element for plant growth, however, rapid release of this element into soil has some serious economic and environmental concerns including ammonia volatilization, nitrate leaching, groundwater contamination, soil acidification, heavy metal contamination, and eutrophication (Lawrencia et al., 2021). Therefore, it is necessary to find an innovative and effective technique that can control all the NPK releases (particularly, nitrogenous amide dissolution) from CMB to maximize the potential of biochar-based circular fertilization.

To control or slow down the nutrient release from chemical fertilizers, many formulations have been developed so far. However, an effective slow/controlled-release fertilizer should not be expensive, toxic, short-lived, or imperishable (Lawrencia et al., 2021). Superabsorbent polymer-hydrogel-based fertilizers are sophisticated products that meet the above-mentioned criteria and supply multidimensional benefits. For example, this polymers-based cross-linking formulation can be used both as coating material and carrier-matrix and can improve nutrient release behavior (Sim et al., 2021). Recently, chitosan (a natural biopolymer derived from shells of crustaceans) has been reported to be used as an effective coating and/or hydrogel-forming material. Most importantly, it has the ability to form grafts with some components of CMB, which might help to efficiently retard N release.

Therefore, this study hypothesized that coating CMB by chitosan will delay the release of nutrients, especially nitrogen. Additionally, microwave irradiation-induced grafting between CMB and chitosan will form a durable coating.

Materials and methods: To coat the pristine and Ca-bentonite added CM biochars, the reagent grade chitosan was collected from FUJIFILM Wako Pure Chemical Corporation, Japan. Initially, 5g of CMB or B25CMB was taken in a round glass container and gently mixed with an adequate amount of chitosan solution to get a coated product. Microwave irradiation was applied to part of the chitosan-coated (moist) CMB or B25CMB to promote durable coating between biochars and chitosan. Later, pristine, chitosan-coated and microwaved chitosan-coated biochars were subjected to a hydrostatic nutrient release test.

Results and discussion: The chitosan coating on both CMB and B25CMB promoted beneficial granulation. Moreover, easily soluble primary amides on CMB are transformed into less soluble forms by irradiation-induced grafting. The hydrostatic nutrient release test demonstrated that chitosan-coating (without pH adjustment) and additional microwave irradiation progressively retards the N and K release from CMB, but unfortunately accelerate N and P release from B25CMB. Enhanced P release from B25CMB was minimized by adjusting the pH (6.25) of chitosan. In general, microwaved chitosan-coated CMBs showed a remarkable effect in retarding NPK dissolution, however, the coating was not much efficient for B25CMB.

Conclusion

The findings of this study suggested that low-temperature biochars (≤500 °C), specially those produced from nutrient-rich chicken manure might become comprehensive multinutrient sources and an effective tool for climate-smart nutrient circulation. Knowledge of the nutrient release pattern and transformation mechanism enabled us to understand and predict the fate and transport of those nutrients. Since the initial rapid release of nutrients can lead to loss, environmental pollution, and reduced nutrient use efficiency (NUE), we need to control the release to ensure maximum utilization. The understanding of biochar's nutrient composition and release mechanism helped us to plan strategies to slow down the release up to a certain level. This study further proved that simple and need-based modifications of these BBFs might significantly improve their NUE, ensure the effective circulation of nutrients, and mitigate climate change by sequestering carbon.

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