Parametric and optimization studies on the production of nanoscale biochar-NPK fertilizer using sugarcane bagasse-derived biochar as carrier

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Abstract. Current agricultural practices such as excessive and inefficient application of conventional fertilizers causes serious environmental problems. Thus, this study aimed to produce a fertilizer with nitrogen, phosphorous, and potassium impregnated in an activated sugarcane bagasse biochar which has potential for slow nutrient release. Activated sugarcane bagasse-derived biochar was produced via pyrolysis at 450 ℃ for 1 hour followed by activation using potassium hydroxide. Analysis of the activated biochar showed that it has a high capacity to hold exchangeable cations with a value of 127 mol c/kg soil, high porosity and large surface area (79 m²/g), and high carbon content (77.3% wt). The effects of biochar-NPK ratio (w/w), mixing time, and mixing temperature on the nutrient content of the fertilizer were then evaluated implementing a full factorial experimental design. All main factors were found to be significant on the NPK content of the fertilizer. Optimization runs were subsequently done following Response Surface via Central Composite Design (CCD) to determine formulation conditions for maximum NPK content of the fertilizer. Optimized conditions were 1:2 (w/w) biochar-NPK ratio, 50 ℃ mixing temperature, and 25.60 minutes mixing time. The nitrogen, phosphorous, and potassium content of the fertilizer at optimum condition were successfully verified to be 4.20 %N, 7.57 %P, and 7.01 %K, respectively. The average particle size of the fertilizer was found to be about 2117.2 nm with a polydispersity index of 0.568. The properties of the biochar-NPK fertilizer may be further examined to evaluate its capacity for controlled- or slow-release of nutrients.

Keywords: biochar, sugarcane bagasse, chemical activation, fertilizer

1. Introduction
Agriculture has been one of the essential contributors to the Philippine economy comprising 29 % of the labor force with 11.29 million agriculture-based jobs and this sector is the main source of food and various agriculture-derived products for Filipinos [1,2]. However, the current agricultural systems and practices relies mainly on the use of agrochemicals such as pesticides and synthetic fertilizers without disregarding its negative effects on human health, economy, and the environment [3]. Filipino farmers have been extensively using chemical fertilizers, regulators and pesticides for almost three decades because of lack of practical and feasible alternatives [4]. Under tropical conditions, most of the applied nitrogen, phosphorous, and potassium are not utilized by the plants due to leaching, volatilization, and surface runoffs [5]. Consequently, farmers tend to use excess fertilizers to supply the nutrient demands of the crops, but improper and excessive application of this agrochemical causes land degradation and
insufficient soil fertility. Additionally, excess nutrients from agricultural procedures become pollutants in the environment.

Biochar is a carbonized material which can be derived from biomass like wood or manure after subjecting it to high temperature under low or no oxygen conditions \[^6\]. It has nanosized pores that improves water retention and adsorb nutrients for the consumption of plants. Additionally, it has the capacity to immobilize pesticides and herbicides, heavy metals and hormones, reduce leaching of nitrates and prevent dinitrogen oxide emissions \[^7\]. Sugarcane bagasse is a good potential feedstock in the production of biochar because it contains high amount of carbon and its supply in the Philippines is about 1.17 million tons annually \[^8,9\]. Experimental studies show that biochar is a good carrier of nutrients for plant nutrition. The application of biochar enriched with ammonium sulfate as the source of nitrogen enhanced the yield and growth of rice, immobilize phosphorous in acidic soils, and can act as carrier for facilitated transport of nutrients \[^10,11\].

Hence, the general objective of this study is to synthesize a nanoscale fertilizer intercalated with nitrogen, phosphorous, and potassium using sugarcane bagasse-derived biochar as carrier and optimize the process conditions to obtain maximum amount of NPK impregnated in the carrier. Using a nanoscale sugarcane bagasse-derived biochar as carrier for NPK will reduce agricultural waste, determine the factors affecting intercalation of nutrients to the carrier, provide efficient nutrient uptake of plants for growth enhancement, minimizing the damaging effects on the environment, and possible development of a controlled release fertilizer.

2. Materials and Methods

This methodology is composed of three main parts. First is the production of biochar from sugarcane bagasse through pyrolysis and its activation using potassium hydroxide (KOH). Second is the parametric study that will determine which among these three factors, biochar-NPK ratio, mixing time, and mixing temperature affect the incorporation of nutrients in the biochar. Finally, the optimization of process conditions to obtain the highest amount of NPK incorporated in the carrier was determined. Sources of the three nutrients nitrogen, phosphorous, and potassium were from urea, calcium hydroxyapatite, and muriate of potash, respectively.

2.1 Production and Activation of Sugarcane Bagasse

The raw bagasse was first sun-dried for 48 hours and then oven-dried at 80 °C for 24 hours followed by grinding using hammer mill at the Agricultural Machinery Division, Institute of Agricultural Engineering, UPLB. The purpose of grinding is to reduce particle size and increase the surface area of the biomass for efficient pyrolysis. Sieving was done to ensure that the particle sizes are approximately uniform at less than 2 mm using standard mesh no. 16. The sieved SCB was stored in an airtight container at room temperature. Thermal decomposition was done using multiple stainless-steel reactors, each with a diameter of 6 cm, height of 7 cm, and thickness of 0.25 cm with a capacity of approximately 27 g of bagasse. Approximately 25 g of dried and sieved SCB was placed inside each reactor to allow enough space for carbonization between bagasse particles and purged using nitrogen gas for 2 minutes. A total of twelve reactors per batch were placed in a furnace and then heated up to 450 °C. Upon reaching the desired temperature, SCB was pyrolyzed for 1 hour and allowed to cool inside until room temperature was achieved. Several batches of twelve reactors for pyrolysis were done to achieve the total amount of required biochar for batch impregnation. All of the produced biochar was mixed thoroughly to ensure homogeneity.

Chemical activation was done using potassium hydroxide (KOH) as activating agent. The SCB-BC produced was crushed and sieved again using standard mesh 16 (~1.2 mm). For every 25 g of SCB-BC, 150 mL of 7 M KOH solution was added in a 500 mL Erlenmeyer flask. The solution was allowed to stand for 2 hours at room temperature to make sure that the activating agent will access the inner part of the biochar. Filtration and drying at 110 °C overnight in an oven were done after activation followed by another carbonization at 450 °C for 1 hour. After cooling to room temperature, the samples were washed with 0.1 M HCl solution followed by deionized water until neutral pH was achieved. Finally, it was dried at 110°C overnight and stored in an airtight container at room temperature. The yield of
resulting activated SCB-BC from the initial SCB-BC was determined and the activated biochar samples were characterized based on morphology, pore sizes, cation exchange capacity, surface area, and functional groups present.

2.2 NPK and Biochar Preparation

The activated sugarcane bagasse-derived biochar (SCB-BC) was prepared to serve as carrier for the nutrients NPK in the form of urea, calcium hydroxyapatite (CaHAP), and muriate of potash (MoP) respectively. Urea is theoretically composed of 46 % (w/w) nitrogen, calcium hydroxyapatite with 18 % (w/w) phosphorous, and muriate of potash with 49.1 % (w/w) potassium based from the molecular formula of these compounds. Biochar to nutrient ratio was varied in the batch impregnation. However, the ratio of nitrogen, phosphorous, and potassium was fixed at 1:1:1 w/w ratio, respectively. SCB-BC was mixed with the nutrient sources at ratios 1:2 and 2:1 (w/w), respectively. The low level SCB-BC: nutrient ratio was composed of 6 grams SCB-BC and 12 grams nutrient mixture while the high level ratio contained 12 grams SCB-BC and 6 grams of nutrient mixture. Kjeldahl method, colorimetry, and flame photometry were used to determine the approximate amount of nitrogen, phosphorous, and potassium respectively from their corresponding sources. The amounts of nutrient sources needed was computed by dividing the amount of N, P, and K in grams needed for the whole experiment by the experimental percentage of nutrients in urea, CaHAP, and MoP respectively.

2.3 Parametric and Optimization Experimental Design

The study on the incorporation of nutrients to the biochar was composed of two parts-the full factorial experiment where three factors (biochar-NPK ratio, mixing time, and mixing temperature) were evaluated to determine their significant effect on nutrient impregnation; and optimization experiment to generate a model using Response Surface Methodology (RSM), which was used to numerically determine the optimum conditions for impregnation. The parametric study was done by implementing a $2^k$ full factorial design. Three factors namely (1) sugar cane bagasse-biochar-nutrients (SCB-BC:nutrients) (% w/w) ratio, (2) mixing temperature, and (3) mixing time was considered in two levels each. The high and low levels of these factors are shown in Table 1. The ratio of SCB-BC to nutrients as well as the mixing time were based from the study of Tumiao (2018) [12] while the levels of temperature were set to minimize volatilization of ammonia at higher temperatures. Using Design Expert 11, eight treatment combinations were generated with a replicate per run with 4 center points producing a total of 20 runs.

| LEVEL | SCB-BC to Nutrients Ratio (w/w) | Mixing Time (mins) | Mixing Temperature (℃) |
|-------|--------------------------------|-------------------|------------------------|
| High  | 2:1                            | 50                | 70                     |
| Low   | 1:2                            | 20                | 50                     |

The responses that were considered in the factorial experiment are amounts of urea, CaHAP, and muriate of potash impregnated on the biochar in terms of % N-P-K respectively. Total nitrogen was determined using Kjeldahl distillation, phosphorous by colorimetry, and potassium by flame photometry.

For the optimization of the process conditions, Response Surface Methodology (RSM) was used. RSM is a collection of statistical and mathematical techniques that can generate a model of optimized input variables. In this case, Central Composite Design (CCD) was used to develop a second order equation for the response variable even without the use of three level full factorial design. The aim of this optimization was to maximize the total nutrient content in the biochar reported as % N-P-K. The three factors namely biochar-NPK (w/w) ratio, mixing temperature, and mixing time which were all
found to be significant were considered for this part. Verification of the optimum condition was done after the model generation and numerical optimization performing three to five runs at the optimum conditions.

2.4 Batch Impregnation of Nutrients to Biochar

The materials that were used for the nanofertilizer formulation are the activated SCB-BC as carrier and nutrients N, P, and K from urea, CaHAP, and muriate of potash respectively. Three factors namely: SCB-BC:nutrients (w/w) ratio, mixing temperature, and mixing time were varied and observed in the parametric and optimization experiments. The amounts of nutrient mixture and SCB-BC were prepared according to 1:2 and 2:1 ratio with a total of 18 g inside a 250 mL Erlenmeyer flask. 36 mL of deionized water was added to the flask. The mixture was then placed in a hot oil water bath to minimize changes in temperature because water is more volatile than oil and can result to evaporation during mixing. Mixing temperatures were varied from 50 to 70 °C and this range was selected to minimize the volatilization of nitrogen in the form of ammonia at higher temperatures. Mixing time was from 1 hour to 3 hours to allow efficient adsorption of nutrients in the carrier. All treatments were mixed using a magnetic stirrer rotating at a constant rate of 500 rpm. Dissolution of the nutrient sources were done at around 10°C lower than the corresponding mixing temperature and upon dissolution of solids, the temperature was raised to the desired set point and the specified amount of activated SCB-BC was quantitatively added. The mixing time started after the addition of activated SCB-BC. Upon reaching the set mixing time, 1.8 g of starch was added as a binder for the formulations and was allowed to mix for 5 minutes. It was transferred to a petridish and was oven dried at 85 °C for complete removal of moisture. The formulated biochar-NPK fertilizer was crushed to reduce the particle sizes and analyzed using Kjeldahl method, colorimetry, and flame photometry for N, P, and K content, respectively. Also, it was characterized based on morphology, size distribution, surface area, and functional groups present.

3. Results and Discussion

3.1 Yield of Activated Biochar

The thermal carbonization of sugarcane bagasse at 450°C under low oxygen condition resulted to the production of biochar- a material that is commonly used as an adsorbent and soil enhancer. Approximately 24.86 g of dried and milled sugarcane bagasse was pyrolyzed per reactor producing around 6.23 g of biochar which corresponds to biochar yield of about 25.11 % w/w. This value is comparable to the results obtained by Saleh and Hedia (2018) [13] wherein they obtained around 25.58 % w/w biochar from sugarcane bagasse at 500°C for 60 minutes. The mass reduction of sugarcane bagasse may be attributed to the release of gases and volatile organic compounds from the biomass during pyrolysis leaving mostly fixed carbon and ash in the residue. After chemical activation using potassium hydroxide, the yield of activated biochar from the raw biochar was calculated to be about 54.29 % w/w on the average. This corresponds to an overall yield from bagasse to activated biochar of about 13.65 % w/w. Figure 1 displays the changes in the appearance of raw bagasse after pyrolysis and chemical activation.

Figure 1. Raw bagasse (left), biochar (middle), and activated biochar (right).
Figure 1 clearly shows the drastic physical change from raw sugarcane bagasse to activated biochar. The initial dried bagasse has a very rough texture, less dense and bulky, and light brown in color while the biochar from bagasse (before activation) has also a rough texture; however, it became more bulky and lighter in terms of mass and its color is black. The KOH-activated biochar, on the other hand, has a very smooth texture, denser, and darker in color than the raw biochar. Black color can be associated to the high amount of fixed carbon that remained since most of the volatile and combustible gases like hydrocarbons were removed during pyrolysis. These physical changes may be caused by the thermochemical decomposition of bagasse due to high temperature. According to Zafar (2009) [14], the components that are being removed during pyrolysis are mostly gases like hydrogen, methane, carbon dioxide, and carbon monoxide leaving the char and bio-oil. He added that the process will yield more biochar if the temperature is less than or equal to 450°C. Zaini and Hui (2015) [15] stated that potassium hydroxide (KOH) is usually used in the production of activated carbon since it can produce good pore development and high specific area compared in using zinc chloride and phosphoric acid. This is caused by the pore development that hastens loss of carbon due to the intercalation of potassium ions in the carbon network. Potassium hydroxide also dehydrates the biomass during carbonization.

3.2 Biochar-NPK Fertilizer Yield

Biochar-NPK fertilizer were formulated by mixing nutrient sources of nitrogen, phosphorous, and potassium with activated biochar at varying biochar-to-nutrient ratio, mixing time, and mixing temperature. The mixtures were dried and the resulting yield of the fertilizers from their components was about 90.26 % by weight on average. The decrease in the amount of mixed fertilizer components maybe due to the dissolution and evaporation of nutrient sources at relatively high temperatures which was evident due to pungent odor of gaseous ammonia escaping during mixing and drying. Figure 2 shows the image of the formulated biochar-NPK fertilizer. The formulated fertilizer as shown above has smoother texture compared to the activated biochar; it is also denser and more grayish in color due to the incorporation of mixed nutrients. Initially, it is compact after drying because of the starch added but it can be easily powdered using mortar and pestle. A relatively low drying temperature (85 ℃) may have contributed to a high fertilizer yield, thus preventing possible losses of nutrients.

Figure 2. Dried biochar-NPK fertilizer.

3.3 Effect of Biochar-NPK Ratio

Based from the model and the results of the ANOVA, the most significant factor in the factorial experiment in determining the nutrient content of the fertilizer is the biochar to NPK ratio (p<0.0001). A general negative trend was observed for all nutrients as the amount of biochar is increased; consequently, as the amount of biochar is decreased, the individual amounts of N, P, and K increases. At low biochar-NPK ratio, more nutrients are available for impregnation while at high ratio, more sites are available for adherence of nutrients. If the values of the center points were to be ignored, treatments with 1:2 ratio have the highest %N. The same trend was observed in the phosphorous content; the lower the amount of added biochar, the higher the phosphorous content of the fertilizer. According to Laird
et al. (2010) \cite{16}, since phosphorous occur in fertilizers or soils as phosphate ions, biochar with high cation exchange capacity helps in the retention of P and enhances its activity with cations. Finally, the biochar-NPK ratio also has the largest effect on %K. As the amount of biochar is increased, the amount of potassium in the fertilizer decreased. Potassium ions are the usual ions attracted in the biochar since they are easily adsorbed and increasing the amount of nutrient mixture directly affects the potassium concentration adsorbed.

3.4 Effect of Mixing Temperature
Analysis of the generated plots showed at the low biochar-NPK ratio (1:2), the amount of nitrogen and phosphorous content of the formulated fertilizer decreases after increasing the mixing temperature from 50 °C to 70 °C. The only responses considered were %N and %P because the term B-mixing temperature is not present in the model for %K. Temperature was observed to have a negative effect on %N at the temperature range considered. This may be due to the evolution of ammonia gas at high temperatures observed by the presence of pungent odor of gas coming from the formulation at high temperature heating which may decrease the amount of available nitrogen from urea. According to PubChem (2019) \cite{17}, urea (NH2CONH2), also known as carbamide is a nitrogenous compound containing two amine groups(-NH2) and a carbonyl group (C=O). It has a colorless, crystalline structure which melts at 132.7 °C and decomposes before boiling. The decomposition of aqueous urea according to Gargurevich (2016) \cite{18} happens in two steps, forming an intermediate called ammonium carbamate (NH4COONH2) and the reaction is given in the Equation 1.

\[
\text{NH}_2\text{CONH}_2 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{COONH}_2 \rightarrow 2\text{NH}_3 + \text{CO}_2
\] (Equation 1)

The pungent odor of ammonia (NH3) was first observed at higher mixing temperature of 70°C and was more evident during drying at 85°C. Moreover, Sung et al. (2004) \cite{19} studied the thermal decomposition of urea and their experiment showed that higher temperatures lead to significant conversion of urea to ammonia. Moreover, Pearson and Smith (1943) \cite{20} presented that temperature significantly affects the decomposition of urea to ammonia because the amount of ammonia formed was increased after increasing the temperature. This phenomenon must be prevented in formulation of fertilizers since the goal is to capture nitrogen and maximize it in the fertilizer formulation for plant usage.

On the other hand, %P increases as temperature increases. Trazzi (2016) \cite{21} presented that the temperature increases the adsorption of phosphate ions in biochar since high temperatures favor the reactivity of surface sites and pores of the adsorbent. Finally, he also said that temperature enhances the intraparticle diffusion of sorptive phosphate ions since it also increases the diffusion of molecules in the pores of the adsorbent, in this case activated biochar.

Potassium chloride (KCl) is the most common and widely used source of potassium in fertilizers because of its abundance, relatively low cost, and higher potassium content with an experimental value of 52 % K. This compound dissolves readily in water with a solubility of 344 g/L at 20°C however, the effect of temperature in the potassium content in the fertilizer was found to be not significant. This is because KCl is not volatile and does not decompose into volatile compounds; its melting point is 770°C and boiling point of 1420°C. Hou et al. (2015) \cite{22} studied the behavior of potassium ions adsorbed in activated carbon and they showed that there is no specific trend for the potassium content in the level of temperatures that they have considered (10 to 80 °C). Furthermore, the temperature 60 to 80 °C improves the activity and energy of potassium ions, accelerating the movement of ions in solutions which may adsorb and remove the ions in the activated carbon at the same time.

3.5 Effect of Mixing Time
Mixing time of biochar and nutrient sources were varied in the factorial experiment with a low level of 20 minutes and high level of 50 minutes while in a heated oil bath with varying temperatures. Based on the result of the ANOVA, mixing time appeared to be significant on the amount of nitrogen (p=0.0046) and phosphorous (p=0.0147), but not on potassium (p=0.5572). From the results, the trend implies that higher mixing time results to lower amounts of nutrients in the fertilizer. For nitrogen content,
Manikandan and Subramanian (2013) [23] shows continuous mixing in formulating controlled-release fertilizers and Senda et al. (2009) [24] stated that high rotational speed of mixing leads to shorter mixing time requirement to impregnate the nutrients. These related studies imply that mixing time are not a major factor in the nutrient content of the formulations; however, it still appears to be significant in the factorial experiment and this may be caused by the escape of nitrogen as ammonia due to prolonged mixing. Senda et al. (2009) [24] also showed that longer mixing time may result to desorption of urea and decrease the nitrogen content. Mixing time was also found to be significant in the model for %P, and the plot shows that longer mixing time results to lower %P. Hale et al. (2013) [25] studied the desorption of phosphate-P and their results showed that longer residence time results to desorption of phosphorous. On the other hand, the effect of mixing time for potassium content was found to be insignificant with a p value of 0.5572. This may be because the potassium ions in the formulation are readily attached in the biochar and does not form volatile potassium-containing compounds that may be removed during longer periods of heating.

3.6 Coded Equation of the Main Factors in RSM

The 23 full factorial experiment with 4 center points revealed that factors such as biochar-NPK ratio, mixing temperature, and mixing time have significant effects on the concentration of nitrogen, phosphorous, and potassium in the formulated fertilizer. Moreover, addition of center points improved the design by incorporating curvature terms and since all the responses have significant curvature, the design was augmented using face-centered Central Composite Design (CCD) using the given significant factors. Three coded equations for the responses were generated in the analysis of the data. Equation 2 shows the coded equation that can predict the %N within the given levels of factors.

\[
%N = 4.13 - 0.78A - 0.24B - 0.29C + 0.21AB - 1.21A^2 - 0.41C^2 \quad (Equation \ 2)
\]

The coded equation for nitrogen is generated with no transformation and its value is calculated directly from the given equation with the biochar-NPK ratio having the highest negative effect on %N followed by mixing time and last is the mixing temperature with the least negative effect. The only factor with positive effect is the interaction AB (biochar-NPK ratio and mixing temperature). This equation also has quadratic terms which are not available in the factorial experiment. These terms amplify the negative effect of the main factors A and C. The quadratic terms A^2 and C^2 imply that at very high levels of biochar-NPK ratio (A) and mixing time (C) respectively, these factors will have a dominant negative effect on the nitrogen content. Also, Equation 3 below shows the coded quadratic equation for %P which can be used to predict the values within the levels of given factors.

\[
%P = 5.84 - 1.98A - 0.61A^2 + 0.78C^2 \quad (Equation \ 3)
\]

The coded equation for %P was also generated without transformation and the biochar-NPK ratio (A) term has also the greatest negative effect on the amount of P followed by the quadratic term A^2. The terms B, AC, BC, and C^2 has positive effects on phosphorus although the quadratic terms is the only significant in the model which is not available in the equation for the factorial runs. Finally, the coded equation for %K is given by Equation 4.

\[
%K = 5.4 - 1.52A + 0.3C + 0.32AC - 0.9C^2 \quad (Equation \ 4)
\]

The terms with a significant negative effect on %K are A and C^2 while the term AC has the only significant positive effect. The quadratic term from this equation imply that at very high mixing time, the term C will have a dominant negative effect on the potassium content.

3.7 Numerical Optimization

In determining the maximum amount of nutrients impregnated in the carrier, numerical optimization was employed. The three factors that were considered are biochar-NPK ratio, mixing temperature, and mixing time. The responses namely %N, %P, and %K were all set to maximize within the level of factors considered. Table 2 shows the condition of formulation to maximize NPK content in the fertilizer.
Additionally, it can be observed that the optimum conditions have two factors at the lowest level set in the experiment; this is because of the effect of the optimum conditions for phosphorous and potassium since the red region of their response surface is on the edge of the levels of factors considered. This condition has a desirability of 0.858 with predicted values of 4.18 %, 7.65 %, and 6.75 % for nitrogen, phosphorous, and potassium respectively. The optimum conditions generated were experimentally verified using 3 trials to determine if the model and optimized condition are valid. Table 3 shows the summary of the results of verification experiment.

From the table above, all of the calculated experimental values of the nutrients agree with the predicted values since their corresponding percent differences are less than 10%. After nitrogen analysis using Kjeldahl method, it was found that 4.20 % is the nitrogen content of the formulated fertilizer at optimum condition with 0.48 % difference to the predicted mean value of 4.18 %N. On the other hand, the calculated experimental value for %P is 7.57 % giving 1.05 % difference on the predicted value of 7.65 %P. Finally, the average potassium content of the fertilizer at optimum condition is 7.01% which is 3.85% higher than the predicted value of 6.75 %K. Statistical analysis from the post analysis indicates that the nitrogen, phosphorous, and potassium content of the fertilizer formulated at optimum conditions are expected to fall within their corresponding ranges with lower and upper bound 95 % of the time.

### 3.8 Characteristics of Biochar and Biochar-NPK Fertilizer

Elemental composition of the biochar, which was analyzed using Energy Dispersive X-ray Spectroscopy revealed that the carbon content of the sample is about 77.3 % with 19.8 % oxygen, 0.04 % aluminum, 0.57 % silicon, and 2.28 % potassium. The high amount of carbon in the sample may be caused by the fixed carbon content of the biomass and the potassium content resulted from the addition of potassium hydroxide as activating agent. The results of the FT-IR for the activated bagasse biochar showed that there is presence of secondary N-H group stretching at medium intensity for wave range of 3300-3350 cm\(^{-1}\). The next peak is at the range of 2300 to 2400 cm\(^{-1}\) which indicates a strong intensity of stretching O=C=O (carbon dioxide) bond. Additionally, the peak at 1550 to 1600 cm\(^{-1}\) corresponds to N-H (amine) bending at medium intensity, and the final peak at 1350 to 1400 cm\(^{-1}\) shows O-H (alcohol) bending at medium intensity. These functional groups are highly polar and they may form bonds with the compounds or functional groups in the added nutrients.

According to Hazleton and Murphy (2007) \([26]\), cation exchange capacity (CEC) is the measure of capacity of a material to hold positively charged cations and it is important in relation to structural
stability, nutrient availability, and reaction to fertilizers. The analysis done showed that the activated bagasse biochar has a high value of CEC which is 127 mol e/kg biochar and it is comparable to the material vermiculite which is the second material to have the highest CEC in the soils. Also, this high value of CEC indicates that more cations such as $K^+$ and $NH_4^+$ may be adsorbed in the activated biochar, thus efficient retention of nutrients. On the other hand, Figure 3 shows the SEM micrographs of the activated biochar using a Zeiss Ultra Plus Field Emission-Scanning Electron Microscope in high vacuum mode at an acceleration voltage of 5 kV.

![SEM image of activated biochar at 1300x (left) and 52130x (right) magnification.](image)

The SEM micrographs above show that the activated biochar has a very porous structure which corresponds to high specific surface area and more nutrient-attachment sites as carrier of fertilizer. The nitrogen sorption analysis revealed that the surface area of biochar is 66.6 $m^2/g$ and 79 $m^2/g$ for the activated biochar. This clearly indicates that the activation using potassium hydroxide (KOH) resulted in increasing the specific surface area and porosity of the material; thus, making more sites for nutrient loading/adsorption. The surface areas obtained are also higher than the surface areas of biochar from the study of Saleh and Hedia (2018) \cite{13} which are 39 $m^2/g$ and 42 $m^2/g$ for raw and activated biochar, respectively which were used to adsorb phosphate and ammonium ions.

Dynamic Light Scattering (DLS) analysis was done on the biochar-NPK fertilizer formulated at optimum condition to determine its particle size. From the calculated results, it was found that the fertilizer has large particle sizes with peaks sizes of 781 nm and above. The peaks also converge to a z-average value of 2117.2 nm which is relatively high due to the presence of aggregates caused by the addition of starch as a binder. The fertilizer has a polydispersity index value of 0.568 indicating that it has a slightly narrow particle size distribution or more uniform size of particles.

### 3.9 Preliminary Cost Estimation and Analysis

The fertilizer that was formulated at optimum condition (1:2 biochar-NPK ratio, 50°C, and 23.59 mixing time) was used for cost analysis and marketability of the product. The yield of the fertilizer is accounted in the calculations since there is only 89.87 % mass recovered due to losses during formulation. The cost analysis showed that the price of 303 g of activated biochar is estimated to be 26.51 PhP (Philippine peso) and this was used on the cost analysis for the production of the fertilizer. The price per kilogram of fertilizer at optimum condition is around 223.86 PhP and its price per sack (50kg), accounting the production yield is about 12 254.66 PhP which is 12 times more expensive than the complete fertilizer used by farmers (1148 PhP). This is mainly because of the price of calcium hydroxyapatite which is the highest contributor to the production cost accounting 85 % of the total cost. A cheaper source of phosphorous may be utilized or a commercial grade and not technical grade CaHAP may also be used to dramatically decreased the production cost.

### 4. Summary and Conclusion

This study focused on the production of biochar-NPK fertilizer using activated biochar from sugarcane bagasse as carrier of nutrients. Biochar was produced by thermal carbonization of bagasse or pyrolysis using a muffle furnace, and it was chemically activated using potassium hydroxide (KOH). The activated biochar was mixed with a nutrient mixture containing equal proportions of nitrogen, phosphorous, and potassium. A parametric study was done to determine the which of the factors: biochar-NPK ratio, mixing time, and mixing temperature are significant to the nutrient content of the formulation. Response Surface Methodology via Central Composite Design (CCD) was used to generate a model that was utilized to determine the optimum condition of maximum nutrients impregnated in the biochar. The result of the parametric study shows that biochar-NPK ratio, mixing
time, and mixing temperature were all significant factors in the model for %N and %P while the ratio and interaction AC (biochar-NPK ratio and mixing time) are the only significant model terms for %K. It was found that increasing biochar-NPK ratio, mixing temperature, and mixing temperature negatively affects nitrogen content of the fertilizer. Phosphorous content was negatively affected by biochar-NPK ratio and mixing time but increases as mixing temperature increases. Finally, potassium content decreases with increasing biochar-NPK ratio but increases with increasing mixing time. After the analyses of the augmented runs, the condition that will maximize the nutrient content in the formulation was numerically optimized and verified. The optimum condition was 1:2 biochar-NPK ratio, 50 ℃ mixing temperature, and 23.59 minutes mixing time with predicted values of 4.18 %N, 7.65 %P, and 6.75 %K while the experimental means of these nutrients were 4.20 %N, 7.57 %P, and 7.01 %K. The characterization experiments show that the activated bagasse biochar has a very porous structure with high surface area of 79 m²/g, high cation exchange capacity of 127 mol c/kg and contains functional groups like amines and alcohols on the surface which is a good indicator of an adsorbent or carrier. Preliminary costing showed that the price of one kilogram of the formulated fertilizer at optimum condition is 224 PhP.

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