The Influence of ZnCl₂ Activation on Macronutrient NPK Adsorption Simultaneously Using Coconut Shell Biochar for Soil Fertility Improvement

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ABSTRACT. The influence of ZnCl₂ activation on macronutrient Nitrogen, Phosphor, Potassium (NPK) adsorption simultaneously using Coconut Shell Biochar for soil fertility improvement has been conducted. Biochar formation is carried out at temperature up to 500 °C using variation in the concentration of ZnCl₂ 0.5; 1.0; 1.5; 2.0; dan 2.5 M. The biochar formed was characterized using Fourier Transform InfraRed (FTIR) spectroscopy and Surface Area Analyzer (SAA). Whereas NPK analysis has used the Indonesian standard method (SNI 7763: 2018). Based on this research, it was concluded that the greater the concentration of ZnCl₂ activator, indicated that the higher intensity of the spectra of –OH and –NH₂ at wave number 3400 cm⁻¹ and 1600 cm⁻¹. It showed that biochar activation was higher and a more active functional group was opened. Increasing the concentration of ZnCl₂ activator has increased Biochar adsorption of NPK macronutrients. The optimum condition for activation of coconut shell Biochar was activation with ZnCl₂ 2.5 M. The addition of activated Biochar was increased soil adsorption on NPK macronutrients. Biochar addition had increased Nitrogen (N) adsorption up to 23.53%, Phosphor (P) up to 200%, and Potassium (K) up to 41.24%.

Keywords: Coconut Shell Biochar, macronutrients NPK, ZnCl₂

INTRODUCTION

Indonesia has areas that are still classified as dry and barren regions such as Wonogiri, Sragen, Purwodadi, Blora, eastern Pati. The dry and barren land has a low fertility rate which causes very low agricultural productivity and cannot even be planted with food crops. The low soil fertility is caused by low nutrient content in the soil, one of which is the macronutrient elements of Nitrogen, Phosphor and Potassium (NPK). Wijayanti, Susuyo, Kurniawan, & Sukarjo (2018) had explained that land contains chemical compounds as a result of a series of chemical reactions in nature that is strongly influenced by various factors around it, these factors will greatly affect the quality of the content of compounds in the soil. Hawkesford et al. (2012) reported the proportion of macronutrients is 3.5% (> 10 mmol / kg BK or> 1,000 ppm) in the soil. Low organic matter such as NPK macronutrients is one of the main problems that causes low productivity of paddy fields. Nitrogen plays an important role in the formation of plant cells, tissues and plant organs. Then, Phosphor is a structural element in nucleic acids and plays a role key in energy transfer as a component of adenosine phosphate. This is also important for the transfer of carbohydrates in leaf cells. Whereas Potassium is an important osmoregulation for cell extension and stomata movement.

Tanasale, Killay, & Laratmase (2012) explained the unfertilized soil is due to low soil ability to macronutrient adsorption by soil and plants. Therefore, efforts are needed to increase the NPK macronutrient content in the soil. One of the efforts that can be done to increase the absorption ability of the soil against NPK macronutrients is by adding adsorbents that can increase the absorption of these macronutrients. Effective adsorbents are adsorbents that have high selectivity and capacity and can be used repeatedly. Pambayun, Yulianto, Rachimoellah, & Putri (2013) reported that one of the effective adsorbents is activated carbon or biocharcoal. Raw materials that can be made into Biochar are all materials that contain carbon, both derived from plants (biomass), animals or minerals. In recent years, there have been many studies on the...
preparation of activated carbon or Biochar and the application of activated carbon from various precursors such as tea residues, orange peels, Coconut shells, Poplar wood, Apricots, Date holes, and Rice husks, Coconut shells (Belaroussi, Seghier, & Hadiel, 2014; Cazetta et al., 2011; Demiral, & Uzum, 2010; El-Dars, Ibrahim, & Gabr, 2014; Gurten, Oznak, Yagmur, & Aktas, 2012; Lapanporo, & Putra, 2013; Bedia, Mirosol, & Cardero, 2010). Praing, Situmeang, & Mahardika (2018) state that Coconut shell is the best active carbon material because it has a lot of micropores, low ash content, high reactivity, and high resistance in the soil. Coconut shell activated carbon can increase the efficiency of using Nitrogen fertilizer (N) and increase the efficiency of water use. Mistar, Ahmad, Muslim, Alfatah, & Supardan (2017) explained that activated carbon consists of 87-97% Carbon and other components are Oxygen, Hydrogen, Sulfur, Nitrogen, and other compounds. And then Idrus et al., (2013) reported that activated carbon has a surface area of about 300 to 2000 m²/g, whereas Esterlita and Herlina (2015) reported that absorption of activated carbon is 82.04% of the weight. Masitoh and Sianita (2013) reported that activated carbon is able to adsorb anions, cations, and molecules in the form of organic and inorganic compounds.

Ramda, Halim, & Handi (2008) explained that carbon can be activated using physical and chemical activation to increase the adsorption ability. The chemical activation process provides many advantages, such as low activation temperature, activation time, activation step, and better porous structure. In this study ZnCl₂ was used because it has several advantages. During the activation process, ZnCl₂ also has functions as a dehydration agent, inhibits the formation of tar, and also directs the reaction of char formation at temperatures below 500 °C. Concentration of ZnCl₂ will affect the character and adsorption ability of Biochar. From the description above, this study aims to determine the effect of ZnCl₂ activation with optimum concentration and composition on Biochar made from Coconut shell as an adsorbent. So that the Biochar can increase the ability to adsorb macronutrients NPK in the soil.

EXPERIMENTAL SECTION

The apparatus was used in this research are Oven, glassware, 80 mesh sifter, FTIR and SAA. Meanwhile, the materials used in this study are dried Coconut shell, ZnCl₂ solution (0.5; 1.0; 1.5; 2.0; and 2.5 M) and 1000 ppm NPK fertilizer solution. Dry Coconut shell is heated at temperatures up to 500 °C under conditions of little oxygen. The Coconut shell charcoal samples produced are then mashed and sieved using 80 mesh sieves. Charcoal is activated using a ZnCl₂ activator solution with a concentration variation of 0.5; 1.0; 1.5; 2.0; and 2.5 M. Activation is done by mixing Coconut shell charcoal in an activator solution with a ratio between the mass of charcoal and activator volume of 1: 4. The mixture is stirred using a magnetic stirrer for one hour. The mixture is then allowed to stand for 24 hours. The resultant activation is washed using distilled water until it is chloride free. Neutral charcoal has been roasted for 180 minutes with a temperature of 110 °C. Then the results obtained will be characterized by FTIR and SAA.

A total of 1 gram activated Biochar of Coconut shell that has been used as adsorbent NPK in 100 ml of 1000 ppm NPK solution for 60 minutes. The optimum ability of activated Biochar adsorption is then used to mix the soil. The Coconut shell activated carbon is used as a soil mixture, with a ratio of 10% activated Biochar and 90% soil used for NPK adsorption to be compared with soil without activated carbon.

RESULTS AND DISCUSSION

Tanasale, Killay, & aratmase (2012) explained the unfertilized soil is due to low soil ability to macronutrient adsorption by soil and plants. Therefore, efforts are needed to increase the NPK macronutrient content in the soil. One of the efforts that can be done to increase the absorption ability of the soil against NPK macronutrients is by adding adsorbents that can increase the absorption of these macronutrients. Effective adsorbents are adsorbents that have high selectivity and capacity and can be used repeatedly. One of the effective adsorbents is activated carbon or biochar. In order to increase the ability of adsorption, Coconut shell charcoal is activated using ZnCl₂ with a concentration of 0.5; 1.0; 1.5; 2.0; and 2.5 M. Then Biochar formed was then characterized using FTIR and SAA. Biochar characterization results are as shown in Figure 1.

Figure 1 shows FTIR spectra of Biochar with ZnCl₂ activator variations. It show a change in absorption peak at wave numbers around 3400 cm⁻¹ and 1600 cm⁻¹ as the concentration of activator ZnCl₂ changed. The spectra at wave numbers around 3400 cm⁻¹ show the overlapping vibrations of the primary -OH and -NH₂ functional groups. While, the spectra at wave numbers around 3400 cm⁻¹ show the bending vibrations of the primary -OH and -NH₂ functional groups. The existence of the -OH and -NH₂ primary functional groups indicates the existence of active groups that play an active role in the adsorption process. The greater of concentration of ZnCl₂ activator, indicate that the higher intensity of the spectra at the wave number around 3400 cm⁻¹ and 1600 cm⁻¹. Therefore, It shows that more and more active groups are open. The greater the active open group is expected to be able to increase the ability of Biochar adsorption of NPK macronutrients. After activation, coconut shell biochar is used for
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Simultaneous (simultaneous) NPK macronutrient adsorption test. The change in NPK concentration between before and after adsorption as seen in Figure 2 until Figure 4.

Based on Figure 2, Biochar’s adsorption capacity increases with an increased concentration of ZnCl₂ activator. However, the concentration of Nitrogen in Biochar without activation, Biochar with a 0.5 M to 1.5 M ZnCl₂ activator obtained a negative change. These mean indicate that the concentration of Nitrogen after adsorption is smaller than before adsorption. This phenomenon is caused by the dissolution of Nitrogen in Biochar. This is due to the adsorption, desorption process, and the relatively weak bond between nitrogen and the active group of the adsorbent. With low activation of ZnCl₂ activator, less open functional groups so that the nitrogen binding process by the adsorbent is weak. This causes the adsorption process to be weaker than the nitrogen desorption process in the adsorbent. wherein, the nitrogen in the adsorbent is the total nitrogen that comes from the adsorbent and the adsorbate solution. While the concentration of Nitrogen in Biochar with activator ZnCl₂ 2.0 M and 2.5 M experienced positive changes. These mean indicate that the concentration of Nitrogen after adsorption is greater than before adsorption. The best condition is Biochar with 2.5 M ZnCl₂ activator which is able to adsorb Nitrogen up to 343.02%.

Figure 1. FTIR Spectra of Coconut shell Biochar with ZnCl₂ activator variations.

Figure 2. The concentration of Nitrogen (N) before and after adsorption (C₀ = Carbon without activation; C-ZC0.5 = activation ZnCl 0.5M; C-ZC1.0 = activation ZnCl 1.0 M, C-ZC1.5 = activation ZnCl 1.5 M; C-ZC2.0 = activation ZnCl 2.0 M; C-ZC2.5 = activation ZnCl 2.5M)
Figure 3. The concentration of Phosphor (P) before and after adsorption (C0 = Carbon without activation; C-ZC0.5 = activation ZnCl 0.5M; C-ZC1.0 = activation ZnCl 1.0 M; C-ZC1.5 = activation ZnCl 1.5 M; C-ZC2.0 = activation ZnCl 2.0 M; C-ZC2.5 = activation ZnCl 2.5M).

Based on Figure 3, Biochar’s adsorption capacity increases with an increased concentration of ZnCl2 activator. However, the concentration of Phosphor in Biochar without activation, and Biochar with 0.5 M ZnCl2 activator experienced obtained negative changes. These mean indicate that the concentration of Phosphor after adsorption is smaller than before adsorption. This phenomenon is caused by the dissolution of Phosphor present in Biochar. While the concentration of Phosphor in Biochar with ZnCl2 activator 1.0 M to 2.5 M obtained positive changes. These mean indicate that the concentration of...
Phosphor after adsorption is greater than before adsorption. The effective condition is Biochar with 2.5 M ZnCl₂ activator which is able to absorb Nitrogen up to 200%.

Based on Figure 4, Biochar's adsorption capacity increases with an increased concentration of ZnCl₂ activator. However, the concentration of Potassium in Biochar without activation, Biochar with a 0.5 M to 1.5 M ZnCl₂ activator obtained negative changes. These mean indicate that the concentration of Potassium after adsorption is smaller than before adsorption. This phenomenon is caused by the dissolution of Potassium in Biochar. While the concentration of Potassium in Biochar with ZnCl₂ activator 2.0 M and 2.5 M obtained positive changes. These mean indicate that the concentration of Potassium after adsorption is greater than before adsorption. The optimum condition is Biochar with 2.5 M ZnCl₂ activator which is able to adsorb Potassium up to 753.33%.

Based on previous results, the optimum biochar is then used as a soil additive to improve the ability of the soil to absorb NPK macronutrients with a composition of 10% Biochar and 90% soil. The results of soil and Biochar-soil adsorption on NPK macronutrients as shown in Figure 5.

Figure 5 showed that the addition of Biochar with optimum activation can increase soil adsorption on NPK macronutrients. The addition of Biochar can increase Nitrogen adsorption by up to 23.53%, Phosphor up to 200%, and Potassium up to 41.24% (Figure 5d). The ability of Biochar adsorption with ZnCl₂ 2.5 M activation is supported by surface area and pore volume as shown in Figure 6.

Figure 6 shows the total pore volume of Biochar with 2.5 M ZnCl₂ activation (0.1896 cc/g) is greater than Biochar without activation (0.1573 cc/g) (Figure 6a). Greater total pore volume causes contact area or surface area is greater. The surface area of Biochar with 2.5 M ZnCl₂ activation (289.4 m²/g) is greater than Biochar without activation (207.7 m²/g) (Figure 6b). This causes the ability of Biochar C-ZC2.5 adsorption (ZnCl₂ activation 2.5M) is greater than the adsorption ability of Biochar without activation. The pore volume and surface area of Biochar will also affect the desorption process as shown in Figure 7.

![Figure 5](image-url)

**Figure 5.** Adsorption of soils and Biochar-Soil to NPK macronutrients (a) Percentage (%) of N, (b) Percentage (%) of P, (c) Percentage (%) of K, (d) Percentage (%) increasing macronutrient NPK in soil after addition Biochar
Figure 6. (a) Pore volume (cc/g) dan (b) Surface area (m²/g) of Biochar

Figure 7 shows that the desorption process in Biochar with activation of ZnCl₂ 2.5M (Figure 7a) is more difficult than Biochar without activation (Figure 7b). This is because the volume of Biochar with activation of ZnCl₂ 2.5M (C-ZC2.5) is greater than Biochar without activation (C0) so the adsorbate that is absorbed becomes higher and more difficult to be released. Absorption at the active site in the pore has the potential for a smaller desorption process than at the surface active site, especially in the physical adsorption process. This is indicated by the volume of N₂ left behind in the Biochar desorption process with 2.5 M ZnCl₂ activation (C-ZC2.5) greater than Biochar without activation (C0). This indicates the ability of Biochar with activation of ZnCl₂ 2.5M (C-ZC2.5) in maintaining NPK macronutrients is greater than Biochar without activation (C0) so that NPK macronutrients are not easily separated.

CONCLUSIONS

Based on the research, it was concluded that the greater the concentration of ZnCl₂ activator, indicated that the higher intensity of the spectra of –OH and –NH₂ at wave number 3400 cm⁻¹ and 1600 cm⁻¹. It showed that biochar activation was higher and a more active functional group was opened.. Increasing the concentration of ZnCl₂ activator has increased Biochar adsorption of NPK macronutrients. The optimum condition for activation of coconut shell Biochar is activation with ZnCl₂ 2.5 M. The addition of optimum Biochar has increased soil adsorption on NPK macronutrients. The addition of Biochar can increase Nitrogen adsorption up to 23.53%, Phosphor up to 200%, and Potassium up to 41.24%.

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