Effect of variations in milling speed with high energy milling treatment on surface area of biochar material

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Abstract. Biochar is a renewable and abundant carbon source and is useful for increasing food security and plant diversity in areas with poor soil conditions, lack of organic matter, lack of water availability and chemical fertilizers. Biochar micro porous structure can be produced from corn cob material which inherits the architecture of raw materials. To increase the surface area of the biochar material, high energy milling treatment was carried out in this study by varying the speed of milling in the same milling time. Milling time is carried out at 3 hours with milling speeds varying of 300, 500 and 700 rpm. The samples were characterized by X-ray diffraction, scanning electron microscope (SEM), particle size analyser (PSA), and surface area analysis - Brunauer, Emmett and Teller (SAA-BET). The test results show that at speed of 300, 500 and 700 rpm it has produced biochar with a particle size of 947.9; 868.5 and 799.2 nm, respectively. While the SAA-BET test has produced a surface area of 10.115; 15.889 and 18.303 m²/g. This study describes an increase of surface area when compared without milling treatment which has a surface area of 7917 m²/g.

1. Introduction

The use of pesticides and artificial fertilizers on agricultural land together can pollute the soil and also agricultural products. Soil contamination is difficult to remove naturally, so remediation technology is needed which can accelerate the degradation process of both pesticide residues and heavy metals. The continuous use of pesticides and artificial fertilizers is believed to leave insecticide residues and certain heavy metals in the soil, water and plant products above. Meanwhile, in various agricultural lands, a number of contaminants from the insecticide cypermethrin and heavy metal Pb have been found. Contamination of active ingredients and heavy metals is difficult to decompose naturally, so remediation is expected to be a solution in reducing the two contaminants. The pyrethroid class of pesticides can reduce the production of estradiol [1] and can cause estrogenic effects in female mammals and antiandrogenic in male mammals [2].

To prevent further impacts of pesticide residues and heavy metals, land remediation can be carried out. Remediation by using a number of ameliorant materials processed from agricultural waste is believed to reduce pesticide residues, but also to increase soil fertility and land productivity. Biochar is a promising solution to remediate heavy metal contamination. Biochar is solid carbon from pyrolysis process of biomass under limited oxygen or vacuum conditions. Biochar can be formed from plant and animal biomass, livestock manure, and most of the biomass residues of living things [3].
Biochar has the potential with a large surface area, very porous morphology, its functional groups have the potential to reduce bioavailability and leaching of heavy metals through adsorption and other physico-chemical reactions and can also increase soil fertility and improve soil properties [4]. Biochar can absorb anions, cations and molecules in the form of organic and inorganic compounds, solutions or gases [5]. The potential of biochar to eliminate the toxicity of heavy metals has been tested. The research was carried out by biochar treatment on soil contaminated with heavy metals in mining waste. The result was a decrease in the bioavailability of Cd, Pb, and Zn. However, the rate of decline was still relatively small and only focused on Cd. This is because there are no other physical characterizations that have been carried out to increase the absorption rate of the biochar used [6]. Pretreatment with phosphoric acid activating agent has been carried out on biochar from corn cobs and its application in soil improvement is used as an adsorbent to remove Cr (VI) from aqueous solutions [7].

The physical characteristics of biochar play an important role in reducing the metal content in the soil. One of these characteristics is the size of the biochar. Based on the reaction rate theory, it states that the smaller the particle size, the wider the surface area, so that the absorption rate is higher. This is because the small particle size has greater inter-molecular energy so that the absorption is better. There are two general processes for obtaining a nanometer-sized material. The first process, namely by breaking the larger material into smaller pieces mechanically, chemically, or other forms of energy which we usually refer to as the top down process [8]. The second process, namely by synthesizing the material from the form of atoms or molecules through a chemical reaction which we usually call the bottom-up process [9]. The bottom-up process can control the particle size, particle shape, particle distribution, particle composition, and the level of particle agglomeration [10]. In the top down process, the material that was originally micrometer in size is smoothed to obtain a finer material size. This process is carried out by several methods, including High Energy Milling (HEM), mechanical chemical processing, etching, electro blasting, sonification, sputtering, and laser ablation [11]. HEM is considered more practical to reduce the size of biochar particles so that by decreasing the particle size it will expand the surface area and increase the absorption ability of pollutants in the soil [12].

The effect of HEM treatment on biochar as absorbent has not been widely used. Previous studies have been carried out with HEM treatment on hardwood biochar and zeolite have the potential of becoming a carrier material to hold nutrients for effective fertilizer preparation, without any harmful side-effects [13]. Homogenous powder was produced by ball milling technique with four different hours. The particle size distribution has been found that reduced size was observed and surface area increased three fold with decreased particle size after 6 hours ball milling. High speed and long duration improved the nanoparticle production. This study suggests that natural adsorbents have less specific surface area initially which increases significantly after ball milling [13]. In another research, nanobiochar was produced from pine wood biochar using a planetary ball mill. The parameters of ball milling including time, rotational speed and mass ratio of ball to powder to obtain nanoparticles in a short time and at lower energy consumption have been optimized. The results show that the interaction effect of time and rotation speed is a significant contributor to the particle size during milling and the smallest particles are about 60 nm for the optimum parameters of 1.6 hours and 575 rpm. However, size measurements show that the particles have a great tendency to agglomerate. Further studies showed that conditioning of biochar at cryogenic temperatures prior to milling inhibits agglomeration of nanoparticles which are important in industrial processes [14]. Ball milling was used to prepare two ultrafine magnetic biochar/Fe₃O₄ and activated carbon (AC)/Fe₃O₄ hybrid materials targeted for use in pharmaceutical removal by adsorption and mechanochemical degradation of pharmaceutical compounds. Both hybrid adsorbents prepared after 2 hours milling exhibited high removal of carbamazepine (CBZ), and were easily separated magnetically. The research provided an easy method to prepare ultrafine magnetic adsorbents for the effective removal of typical pharmaceuticals from water or wastewater and degrade them using ball milling [15].

In this study, to increase the surface area of the biochar from corncob, high energy milling treatment was carried out by varying the speed of milling in the same milling time. To determine the characteristics of biochar after milling treatment, characterization is carried out using X-ray diffraction (XRD), scanning electron microscope (SEM), particle size analysis (PSA) and Brunauer–Emmett–Teller (BET).
2. Methods
The agricultural waste (corn cob) was used as a feedstock of biochar using slow pyrolysis method with a temperature of 300 °C. This temperature was chosen because the carbonization process of organic matter only started at 220 °C [16]. The combustion process was carried out for 4 hours. This process was carried out to reduce the moisture content. After burning the biochar was then left to stand for 24 hours. Furthermore, the biochar was removed from the reactor and then crushed and sieved with a 2 mm sieve.

The milling process using HEM was carried out by varying the speed of milling in the same milling time. Milling time was carried out at 3 hours with milling speeds varying of 300, 500 and 700 rpm. Milling time of 3 hours was chosen in order to reduce the agglomeration that often occurs when milling is carried out for more than 3 hours. Biochar that has been milled was then sieved using a sieve with a size of 200 mesh so that the size of the biochar particles becomes more uniform.

3. Results and Discussion
The milling process using HEM can break down biochar into smaller biochar particles. This happens because HEM works by destroying the biochar through the collision mechanism of the milling balls. The movement of the ball follows the movement pattern of the container in the form of a three-dimensional ellipse. This collision allows the formation of submicron scale powder particles due to the high frequency of collisions.

The XRD patterns of the biochar is shown in figure 1. The main peaks with the highest intensities are at 2θ=20.86° indicated the presence of carbon and 2θ=26.73° confirming the presence of quartz (SiO₂). The peak at 67.84° indicate the presence of quartz (SiO₂). Sharp and small peak at 50.54° is due to Ca(OH)₂ (JCPDS card no. 01-073-5492). The X-ray diffraction peak confirmed that bio-char possesses a heterogeneous surface.

![X-Ray diffraction of Biochar a) without milling and and with milling of b) 300 rpm, c) 500 rpm, d) 700 rpm.](image)

The SEM micrographs of biochar without and with milling of 300, 500 and 700 rpm are shown in figure 2. SEM images reveal the surface morphology of biochar including the presence of pores and their size with fragments in irregular shape. Biochar that has been processed has small particles that can also be seen and may be the result of crushing the mortar and scratches during handling. The observed carbon particles seemed to shrink with a certain degree of agglomeration with increasing milling time. The
sample observed was a mixture of amorphous and crystalline carbon. Compared with biochar without milling (figure 2a), the particle size of biochar with milling was much smaller (figure 2b, 2c and 2d). Furthermore, the SEM micrograph of biochar with milling of 700 rpm showed a smaller portion of the biochar size compared to biochar milled at 300 and 500 rpm although some of it was agglomerated. This variation showed that the morphological features were strongly influenced by milling process. This result was consistent with values of particle size and surface area.

Figure 2. SEM micrographs of biochar a) without milling and with milling of b) 300 rpm, c) 500 rpm, d) 700 rpm.

Table 1 shows values of particle size and surface area for biochar without milling (#a), with milling of 300 rpm (#b), 500 rpm (#c) and 700 rpm (#d). The results of milling treatment have obtained the smallest biochar particle size of 799.2 nm with the largest area of 18303 m²/g in the milling treatment with a milling speed of 700 rpm.

Table 1. Values of particle size from PSA measurement and BET surface area.

| Code | Sample                | Particle size (nm) | Surface area (m²/g) |
|------|-----------------------|--------------------|---------------------|
| #a   | without milling       | 4.205,2            | 7.917               |
| #b   | with milling of 300 rpm | 947.9              | 10.115              |
| #c   | with milling of 500 rpm | 868.5              | 15.899              |
| #d   | with milling of 700 rpm | 799.2              | 18.303              |

Figure 3 shows graphic of particle size and surface area as the function of milling speed of HEM treatment for biochar of 0, 300, 500 and 700 rpm. It is found that an increase in milling speed from without milling to milling treatment of 700 rpm indicates a significant increase in the BET surface area, from 7.917 to 18.303 m²/g. On the other hand, there was a significant decrease in biochar particle size from without milling to milling treatment at a milling speed of 300 rpm, while an increase in milling speed to
700 rpm resulted in a sloping reduction in particle size. Milling speeds below 300 rpm are not performed because the milling process requires sufficient energy to create cracks in the biochar material. Several studies have shown giving milling speed treatment above 300 rpm to break the biochar material [14,17,18]. At the 700 rpm milling speed showed the smallest particle size is 799.2 nm. The sloping decrease of the biochar particle size due to the increase in milling speed is thought to be due to the agglomeration of the biochar material. The effect of biochar aggregation on the milling process cannot be neglected due to the release of moisture [13].

![Figure 3. Curve of particle size and surface area as the function of milling speed of HEM for biochar of 0, 300, 500 and 700 rpm. The blue point curve shows the change in particle size and the red point curve shows the change in the surface area by the milling speed variation.](image)

4. Conclusion
This study explains that the particle size of the corncob biochar material is reduced by increasing the milling speed. A significant reduction in particle size was observed after 300 rpm milling treatment. This study explains that the particle size of the corncob biochar material is reduced by increasing the milling speed. A significant decrease in particle size was observed after milling treatment at 300 rpm and at an increase to 700 rpm showed a sloping decrease in particle size. This is due to the presence of agglomeration by the release of moisture from the biochar. The results showed that the surface area of biochar significantly increased from 7,917 to 18,303 m²/g.

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