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## Adsorption characteristics of copper ions using biocharcoal derived from nutmeg shell

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Abstract. The objective of this study was to characterize the parameter conditions such as optimum weight, contact time, pH, and concentration of the copper solution upon the absorption of biocharcoal derived from nutmeg shell. The concentration of copper ions was measured at a wavelength of 324.7 nm using an atomic absorption spectrophotometer (AAS). Results showed that the optimum adsorption of Cu(II) ions on the optimum weight of biocharcoal was 125 mg, the percentage of Cu(II) ions adsorption was 95.69%, and the weight of Cu(II) ions adsorbed was 11.48 mg/g. The optimum contact time was obtained at 60 minutes with the adsorption percentage of Cu(II) ions of 98.19%, in which the weight of adsorbed ions was 10.25 mg/g. The optimum pH was obtained at pH 7.0 with the adsorption percentage of Cu(II) ions was 99.95%, with the weight of adsorbed Cu(II) ions was 11.99 mg/g. The optimum concentration was obtained at 20 ppm with the adsorption percentage of Cu(II) ions was 99.75%, whereas the weight of the adsorbed Cu(II) ions was 7.99 mg/g. The maximum adsorption capacity of biocharcoal against Cu(II) ions using the Langmuir isotherm equation was 62.50 mg/g biocharcoal.

#### 1. Introduction

The nutmeg (Myristica fragrans Houtt) is an Indonesian native plant originating from the island of Banda [1]. The nutmeg product is well known in the global market including mace share of 75% and 20%, respectively [2], not only because it has a characteristic, strong fragrance and a warm, slightly bitter taste and high oil yield, but the product can also be processed into economical value products like essential oil for commercial culinary use, medicine and other pharmacological properties [1–3].

The nutmeg shell, which comprised 5.1% of the total fruit weight [4]–[5] is quite less useful though Salindeho et. al [6] have reported the application of nutmeg shell as a raw material to produce liquid smoke for fish preservation and Idris et. al [7] who also utilized the nutmeg shell into briquette. This huge amount of shells has numerous prospectives and commercial values, hence, the research into the best methods to exploit the shell is drawing increasing studies. Alternative use of the shell is the conversion into biocharcoal as a promising adsorbent for heavy metal mitigations [8–12], soil amendments [13–17], and catalyst [18,19]. Biocharcoal is a by-product that is rich in carbon produced from low-temperature pyrolysis of lignocellulosic biomass such as agricultural feedstock and residues, and forestry residues [20]. The nutmeg shell contains lignin (50-59%), cellulose (11-28%) and hemicellulose (9-16%) [4,21].

The productions of biocharcoal from local biomass resources have been performed on durian barks [22], banana peel [23], cacao peel [24], rambutan peel [25], and red fruit's peel [26], and all the biochar

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product were appealed to be confirming adsorbent for various metal ions adsorption in water environments.

This paper is intended to describe the adsorption characteristics of nutmeg shell biocharcoal against copper (Cu) ions.

#### 2. Materials and methods

#### 2.1 Production and analysis of biocharcoal

The reagents used in this work were all available commercially. Nutmeg shell in this study was collected from the local area of Buol, Sulawesi Tengah, Indonesia. The production of nutmeg shells biocharcoal was carried out by modifying the work procedures by Napitupulu., et al [22]. The biochar was then grounded to a particle size below a size of 70 mesh, then stored in a dry closed place and further examination for the biochar characteristics. The surface morphology and quantitative chemical analysis of the biochars were investigated by Scanning Electron Microscopy and Electron Dispersive X-ray (SEM/EDX), which was conducted at LPPT UGM-Yogyakarta using EDXRF spectrometer-JED 2300 Analysis Station, JEOL Ltd. The results obtained from the SEM were in mass percent as processed with the SMILE VIEW. All the absorbances of the solutions were measured using AAS (GBC 932 AA) at a wavelength of 324.7 nm with acetylene-air flame.

#### 2.2 Characterization of biocharcoal

Biocharcoal in four 100 mL-Erlenmeyer each contains 50, 75, 100, 125, and 150 mg mixed with 25 mL of 60 ppm copper solution at pH 6. The Erlenmeyer was then shaken for 30 minutes, then let stand for 24 hours. The filtrate and residue were separated for its adsorption measurement against biochar weight.

The effect of contacting time was performed through which 125 mg of biocharcoal each mixed with 25 mL of 60 ppm copper solution at pH 6 in four 100 mL-Erlenmeyer which then shaken with a variation of time viz. 30, 60, 90, and 120 minutes then let stand for 24 hours.

For pH variation on the copper ion adsorption, 25 mL of copper solution with a concentration of 60 ppm in 3 Erlenmeyers with a pH of 6.0; 7.0; 8.0 and 9.0 were added HNO<sub>3</sub> or NH<sub>4</sub>OH. Each copper solution was mixed with an optimum weight of 125 mg of biocharcoal in a 100 mL Erlenmeyer tube. The Erlenmeyer was covered with aluminum foil, then shaken for 60 minutes, then let stand for 24 hours.

The character of a copper solution of the adsorption process was achieved in which 25 mL of copper solution with a concentration of 10, 20, 30, and 40 ppm in four 100 mL- Erlenmeyer and set the pH to pH 7 from the previous step by adding HNO<sub>3</sub> or NH<sub>4</sub>OH. Each copper solution was mixed with an optimum weight of 125 mg of biocharcoal in a 100 mL Erlenmeyer tube. Erlenmeyer covered with aluminum foil and tied with rubber, then shaken for the optimum minute, namely 60 minutes, then let stand for 24 hours.

Data obtained from the measurement of copper ion concentration using atomic absorption spectrophotometer (AAS) were analyzed using the following equation [27]:  $C_b = (C_i - C_{eq})$  and %Cu absorbed =  $C_b/C_i \times 100\%$ ; where  $C_b$  is the absorbed Cu concentration (mg/L); Ci is the initial concentration of the solution (mg/L), and  $C_{eq}$  is the final concentration of the solution (mg/L).

#### 3. Results and discussion

#### 3.1 Biocharcoal analysis

The contents of carbon, oxygen, and nitrogen in the nutmeg shell biocharcoal (taken from biochar SEM image at magnification 2000×) are C, 49.8%; O, 24.69%; and N, 17.49%, respectively. Some major minerals are Zr, 3.27%, Ca, 2.61%, and Mg, 1.77% respectively (Figure 1). These findings have shown that in the biocharcoal samples, carbon was the main element along with oxygen and nitrogen, which could derive from oxygen-containing functional groups (such as carbonyl or carboxylate) or oxygen-containing particles of metal minerals (such as oxide or carbonate). Scanning electron microscope imaging at various magnification showed that the biocharcoal maintains its original pores structure.

Blurry images were observed as consequences of charge accumulation on the surface of the sample (Figure 2(c)).



Figure 1. Percentage of carbon, oxygen, nitrogen, and some minerals content by SEM-EDX analysis of the nutmeg shell biocharcoal.





#### 3.2 Adsorption characteristics

In this study, the adsorbent weight variations were used, namely 50, 75, 100, 125, and 150 mg (Figure 3(a)). The maximum adsorption capacity showed the maximum ability of nutmeg shell biocharcoal to recovered Cu metal ions until it reached a saturation point at 125 mg Based on the data in Figure 3(a), the adsorbent weight increases from 50 mg to 125 mg, increasing the percentage of copper metal that is absorbed, but at 150 mg adsorbent weight the absorption is relatively decreased. The increase in adsorption was due to an increase in the amount of biocharcoal which interacted with the copper ion. There was an increase in copper ion adsorption at the weight of biocharcoal 50-125 mg because the density of the biocharcoal cells in solution resulted in fairly effective interaction between the active centers of biocharcoal interact. Therefore, when the amount of biocharcoal is enlarged, the ratio is no longer fulfilled, which affects the copper ion uptake activity by biocharcoal [28]. The results obtained indicate that the optimum adsorption of copper ions occurred at 125 mg by weight of biocharcoal with an absorption percentage of 95.69%. This is due to the increase in weight of the nutmeg shell biocharcoal is proportional to the increase in the number of particles and the surface area of the nutmeg shell

biocharcoal so that it can cause an increase in the active site of the adsorption and the absorption efficiency can increase, while the absorption capacity decreases with the increase in the adsorbent [29].



**Figure 3**. The relationship curve of Cu absorbed with (a) the weight of biocharcoal, (b) contact time, (c) pH, and (d) copper solution concentration.

Determination of the optimum contact time for copper ion adsorption using biocharcoal adsorbent from nutmeg shell which was made in variations of time 30, 60, 90, and 120 minutes. Figure 3(b) displays that the optimum contact time attained in the process of varying contact time was 60 minutes, where the percentage of copper ion uptake by nutmeg shell biocharcoal at each time variation was at 30 minutes (96.79%), 60 minutes (98.19%), 90 minutes (94.42%), and 120 minutes (96.78%), respectively. In the time range from 30 to 60 minutes, the ability of the nutmeg shell biocharcoal adsorbent to adsorb copper metal increased, and at 90 minutes the absorption decreases. The results may be elucidated that in the first minute the copper ion absorption is relatively increased because the association between metal ions and the adsorbent take places effectively, since all the active sites in the nutmeg shell biocharcoal bind to each other with copper ions in the solution in term of electrostatic force [30]. The adsorption mechanism is affected by the adsorbent size, which can cause the area of surface interaction to be relatively large, so it allows the active site of the adsorbent to interact very effectively with metal ions. [31]. The longer the time, the more the interaction occurs until a certain time it reached the maximum percentage, and then it declines. The data showed that the optimum contact time occurred at 60 minutes with an absorption percentage of 98.19% and an absorption capacity of 10.25 mg/g which presumably because of the desorption process. This is a phenomenon in physical adsorption which states that the adsorption process is reversible [32].

The removal of Cu(II) ions had shown (Figure 3(c)) an increase from 13.1% to 98.7% with an increase in pH from 6.0 to 7.0 and thereafter remained ascertainable (98.7–99.4%) over the pH range of 8.0–9.0. The effect of pH may likely be clarified as follows: at low pH values, a higher concentration of H<sup>+</sup> ions existing in the reaction mixture contends with Cu(II) ions for the adsorption sites, resulting in

the reduced Cu(II) uptake. As the pH increases, the concentration of H<sup>+</sup> ion decreases, whereas the concentration of metal ions remains constant and therefore maximum uptake of Cu(II) ions is observed.

The acidity degree is a factor that greatly affects the adsorption mechanisms of metal ions in solution [33]. Such a trend was attributed to the increase in proton or ions hydrogen which is the principal control variable, that influences both extractability of metal ions as well as the separation of metals. Also, pH affects the ionic species present in the solution so that it will affect the ion interaction with the active adsorbent site [34]. Determination of the optimum pH in research on copper ion adsorption by nutmeg shell biocharcoal was carried out at variations in pH 6.0; 7.0; 8.0 and 9.0 (Figure 3(c)). This pH influence aims to determine the optimum pH of the copper ion solution adsorption by biocharcoal. In Figure 3, it can be seen that the adsorption of copper ions is influenced by the pH of the solution where at pH 6.0 to pH 7.0 there is a high enough adsorption increase in copper ion with a percentage of adsorption from 98.81% to 99.95%, and after pH 7.0 adsorption. Copper ion decreased rapidly with an absorption percentage of 99.11% and again increased at pH 9 with an absorption percentage of 99.79%. Optimum adsorption power is at pH 7, which can adsorb as much as 99.95% copper.

The ability of an adsorbent is influenced by the concentration of the metal ion solution. Determination of the optimum solution concentration by the nutmeg shell biocharcoal adsorbent against copper ion adsorption was carried out at various concentrations of 10, 20, 30, and 40 ppm. As can be seen from Figure 3(d), copper ion adsorption has increased from 10 ppm to 20 ppm with the percentage of adsorption of 99.63 and 99.75%, respectively. Furthermore, at a concentration of 20 ppm to 40 ppm, the absorption efficiency decreased to 99.48%. The adsorption was influenced by the concentration of the solution, where the greater the concentration of the solution, the copper ion adsorption will also increase to a certain concentration limit [35]. In this case, biocharcoal has not been saturated with copper ions, subsequently increasing the concentration of copper ions, the amount of substance absorbed increased gradually until it reached saturation with metal ions.

#### 3.3. Copper ion absorption capacity

The kinetics of copper ions adsorption utilizing biocharcoal was analyzed with the Langmuir adsorption isotherm equation. This model is subjected to several postulations: the adsorbent surface is homogeneous, consequently, the adsorption energy is constant throughout, each atom is adsorbed on the adsorbent surface at a certain site, and only one molecule or atom can accommodate each part of the surface [36,37]. Adsorption isotherm models each adsorbent mass is determined by looking at the value of the coefficient of determination ( $R^{2}$ ) on the adsorption equation. The largest correlation coefficient value indicates that the adsorption process using the adsorbate is following the characteristics of the assumption. The greater the correlation coefficient value indicates that there is a significant correlation between the amount of adsorbate absorbed and the adsorbate mass [38]. As shown in Figure 4 that the linearization of nutmeg shell biocharcoal in adsorbing copper metal ions was a monolayer mechanism, the correlation coefficient  $R^2 = 0.9572$ , absorption affinity (k) was 1.454 and the maximum absorption capacity (am) was 62.5 mg/g.



Figure 4. Langmuir linearity curve for copper ion absorption.

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#### 4. Conclusion

The optimum weight required for nutmeg shell biocharcoal to absorb copper ions is 125 mg, the weight of absorbed copper ions is 11.48 mg/g, and the percentage of absorbed copper ions is 95.69%. The optimum adsorption of copper ions at the variation of contact time occurred at 60 minutes with the weight of absorbed copper ions being 10.25 mg/g, and the percentage of absorbed copper ions was 98.19%. The optimum adsorption of copper ions at various pH occurred at pH 7.0; with the weight of absorbed copper ions are 11.99 mg/g, and the percentage of absorbed copper ions is 99.95%. The optimum adsorption of copper ions at various concentrations occurred at a concentration of 20 ppm with an absorbed copper ion weight of 7.99 mg/g, and the percentage of absorbed copper ions was 99.75%. The maximum absorption capacity of nutmeg shell biocharcoal against copper ions using the Langmuir isotherm equation is 62.5 mg/g of biocharcoal.

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