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EXTRACTION OF THE HUMIC-LIKE SUBSTANCES FROM COFFEE HUSK-DERIVED BIOCHAR: DETERMINE PARAMETERS OF EXTRACT PROCESS

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ABSTRACT

Dissolved organic carbon (DOC) with a humic acid-like composition is a very important component of biochar in agricultural production applications. DOC extraction from biochar derived from coffee husks at different pyrolysis temperatures using a KOH solution was performed. The investigated parameters of the DOC extraction process included biochar pyrolysis temperature (300, 450, and 600℃), KOH content (0.5; 1.0 and 2.0 M), homogenization speed (4000, 6000, and 8000 rpm), extraction time (1, 2 and 3h) and biochar dosage used (50, 100 and 150 g/L). The optimal extraction process parameters were determined based on the DOC extraction efficiency and the contribution of humic acid-like substances. The results showed that the optimal extraction parameters selected were biochar pyrolyzed at 300℃, 2M KOH; homogenization speed of 6000 rpm, extraction time of 2 h, and biochar dosage of 100 g/L. The DOC extraction efficiency reached 33.7% and the main components of DOC were the humic-like substance with high molecular weight. The findings in this study not only determine the optimal parameters for the extraction of organic matter from biochar but also provide a theoretical basis for the use of biochar-based extracts as liquid organic fertilizers or soil conditioners.

Keywords: Biochar, Coffee Husk, DOC, KOH, The Humic-Like Substance.

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INTRODUCTION

The use of biochar in soil C sequestration to improve the fertility of agricultural soils and soil treatment is receiving much attention from agricultural and environmental scientists. Biochar is a carbon-rich solid produced from the pyrolysis of biomass under anoxic conditions.[1] In biochar, dissolved organic carbon (DOC) is the most active and mobile component of interest, which can be rapidly released into the aqueous phase in the soil environment through soil pore water, irrigation, and rainfall.[1] Recommendations suggest that the direct application of too much biochar will reduce its positive effects and may even be harmful to crops and the environment. Therefore, an alternative method to reduce the application rate of biochar could be to use a liquid biochar extract as dissolved organic carbon (DOC).[2] DOC derived from biochar mainly consists of aliphatic compounds, condensed aromatics, phenolics, and polyphenols. The distribution of these components depends on the biochar feedstock and extraction conditions, which can affect the properties of soils and soil ecosystems.[3] The coffee growing area in Dak Lak, Vietnam is constantly expanding, according to statistics in 20121, there were more than 213,336 hectares, with a total output of 526,623 tons of finished beans. Of these, coffee husks account for 40-45% of the weight of coffee beans. In recent years, coffee husks have only been used as soil cover or natural compost, which can easily pollute the environment. This is considered a rich source of raw materials for biochar production, which is the input material for the DOC extraction process. The DOC extraction solution from biochar, commonly used is water or a strong alkaline solution (NaOH or KOH).[4] Which, DOC content, aromatic degree, and molecular weight all increased when extracted with alkali (NaOH or KOH) compared to water.[1,5] DOC is a complex and diverse mixture consisting of truly soluble molecules and colloidal-sized biochar particles.[4,6] Studies have shown that the use of alkaline solutions for extraction results in humic acid-like components being the main ones.[1,7] Therefore, the study will focus on using KOH as the extraction solution instead of NaOH because K is a beneficial element for plants. Many studies have shown that different extraction conditions (such as biochar pyrolysis temperature, extraction temperature, pH, solid-liquid ratio, extraction solution,

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and extraction time) are important in evaluating extraction efficiency and determining the organic matter composition derived from biochar.[7] For example, in the case of biochar extraction from chicken and pig manure, it was shown that the humic acid-like extractable compounds increased at the pyrolysis temperature of 400°C, but when the pyrolysis temperature continued to increase, they decreased again.[1] Meanwhile, the total dissolved organic content DOC decreased with increasing pyrolysis temperature.[1] The DOC content of wood biochar (oak, pine, Chinese bamboo, etc.) is lower than that of herbaceous biochar (cordgrass, soybean, switchgrass, sugarcane bagasse, etc.) and manure biochar (cow dung, cattle manure, poultry manure, etc.).[1] Extraction efficiency and DOC components in the extract solution need to be determined for effective use in agriculture.[4] However, information on the extraction process, extraction efficiency, and humic acid-like components in the extract solution from biochar derived from coffee husks is still lacking. Therefore, the study was conducted.

EXPERIMENTAL

Biochar Preparation

The agricultural waste used in the study was Coffee Husk collected in January 2023 from a household in Krong Buk District, Dak Lak Province. The coffee husks were pre-dried, crushed to <5mm, dried in an oven at 60 °C for 24 hours, and placed in polyethylene bags for storage to prepare biochar. Biochar preparation was performed similarly as in the previous study. The coffee husks were then pyrolyzed in anoxic conditions in a furnace (Nabertherm P330, Germany) at temperatures of 300, 450, and 600°C (Bio 300, Bio 450, and Bio 600) with a heating rate of 10°C/min and kept for 2 hours, then cooled naturally in the furnace.[8] The basic composition of the biochar samples prepared at different pyrolysis temperatures including ash content, volatile matter, and fixed carbon were analyzed by proximate analysis.[1,9]

Experimental Design for Extraction

The extraction process was modified according to the study of Fernández-Delgado *et al.*[10] The extraction parameters such as KOH, biochar dosage, extraction time, and homogenization rate were referred to the study of Cheng *et al.*[4] Specifically, accurately weigh the amount of biochar samples into a 500 mL glass beaker containing 200 mL of KOH solution. The mixture is homogenized on an IKA T25 Digital Ultra – Turrax® (Germany) machine, for predetermined periods. All experiments are conducted at a room temperature of 27±°C. Store the samples in polyethylene bottles and seal them for later analysis. The parameters investigated were: (i) biochar at pyrolysis temperatures (Bio 300, Bio 450, and Bio 600°C); (ii) KOH extraction solution content (0.5; 1.0 and 2.0 M); (iii) Homogenization speed (4000, 6000 and 8000 rpm); homogenization time (1, 2 and 3h) and biochar dosage (50, 100 and 150 g/L). The evaluation parameters were: (a) DOC extraction efficiency; and (ii) the contribution of humic acid-like organic substances in DOC. The principle of selecting the optimal parameters for each experiment was to select the best parameters according to pyrolysis temperature, KOH concentration, homogenization speed, homogenization time, and biochar dosage. All experiments were repeated three times.

Chemicals and Analytical Methods

The chemicals used are all analytical grade from Merk (Germany) such as K2Cr2O7, H2SO4, H3PO4, and FeSO4, and from China such as KOH, and 1,10-Phenanthroline. Determination of total organic carbon (TOC) of biochar and extract solution by Walkley Black method[11,12], Biochar properties include moisture, volatile matter, ash, and fixed carbon content by Proximate Analysis.[1, 9]

Calculation

DOC: Dissolved carbon content, mg/L, Equation (1)

$$DOC\,(mg\ L^{-1}) = \frac{M * C}{V} \tag{1}$$

Extraction efficiency, H%, Equation (2):

$$H = \frac{M * C}{m} 100 \tag{2}$$

Where,
V: volume of extraction solution, L
M: total mass of extraction solution, g
C: DOC content, %
m: mass of biochar used for extraction (dry weight conversion), g
H: Extraction efficiency, %

Qualitative and quantitative identification of organic components contributing to DOC:
The absorbance of the extract solution was measured using a UV-VIS spectrophotometer (GENESY 10S UV-Vis, Thermo – USA). E2/E3 is the ratio of the spectral absorbance measured at 254 and 365 nm wavelengths according to equation (3)[13,14]:

$$E2/E3 = \frac{A_{254}}{A_{365}} \quad (3)$$

Where:
$A254$ and $A365$ are the absorbance at 254 and 365 nm. E2/E3 shows a correlation with aromaticity and molecular weight.[13] E2/E3 decreases as molecular weight increases.[15] The specific UV absorbance at 254 nm (SUVA254) was calculated based on equation (4):

$$SUVA_{254} = \frac{2{,}303 * A_{254}}{L * C} \quad (4)$$

SUV_{254} is the specific UV absorbance, L/(mg m)

L is the length of the quartz cuvette, in this experiment, it is 1 cm. $SUVA_{254}$ represents organic compounds containing aromatic hydrocarbons and double bond or hydroxyl conjugate systems of organic compounds.[15] E4/E5: Determines the relationship between humic and fulvic acids in the extracted solution. E4/E5 is the ratio of the absorbance at 300 nm and 400 nm. It characterizes the degree of humification of the DOC molecule. If E4/E5 is less than 3.5, DOC is mainly composed of humic acids. If E4/E5 is greater than 3.5, the main component of DOC is fulvic acids.[15] E4/E5 decreased, indicating that the humic acidity, aromaticity, and molecular weight of humic substances increased.[16]

$$E4/E5 = \frac{A_{300}}{A_{400}} \quad (5)$$

Experimental Data Processing
The collected data were collected and statistically processed using software in Excel 2016. To minimize sources of error, duplicate samples were used in the analyses to assess precision and bias. One-way ANOVA in SPSS 23.0 was used to determine homogeneity of variance, then determine the difference in mean values between experiments with p-value < 0.05 using Tukey's post hoc test when Sig>0.05 or Tamhane when Sig<0.05.

RESULTS AND DISCUSSION

Some Basic Components of Biochar
The results of determining the basic components in coffee husks and biochar pyrolyzed at different temperatures are presented in Table-1. Specifically, the volatile matter content decreased by 80.6; 61.0; 44.5 and 44.5% for coffee husks, Bio 300, Bio 450, and Bio 600, respectively. This trend is also consistent with previous studies.[17,18] It can be explained that the substances decompose into low molecular weight organic substances or into gaseous form, which are lost when the pyrolysis temperature increases.[18] The weight loss was statistically significant starting from coffee husk, Bio 300, and Bio 450, while the weight loss was insignificant between Bio 450 and Bio 600. This result is also similar to the results of Rafiq *et al.* on biochar derived from corn stover.[18] Fixed carbon content increased with increasing pyrolysis temperature, specifically, fixed carbon content increased by 11.2; 28.2; 39.7, and 38.3% for coffee husk, Bio 300, Bio 450, and Bio 600, respectively. The significant increase from coffee husk to Bio 300 and Bio 450 may be due to the volatile substances being pushed out and the carbon ratio in biochar becoming higher with increasing pyrolysis temperature. While the fixed carbon content of Bio 450 and Bio 600 did not

change significantly, there may have been a transition from amorphous carbon to aromatic and graphic carbon structures, resulting in a higher and more stable fixed carbon residue. The explanation is similar to that in the study of Setyawan *et al.*[17] The ash content increased by 8.2; 10.7; 15.8 and 17.2% respectively. The results were similar to the study of Setyawan *et al.* The ash content of biochar from rice husk, corn cob, and sugarcane bagasse was in the range of 16.00 – 21.17% at pyrolysis temperatures of 400, 500, and 600°C. [17] The results can be explained by the fact that when the pyrolysis temperature increased, the mineral processes occurred, and there was also the decomposition of lignocellulosic substances in the pyrolysis temperature range of 300-400°C.[18]

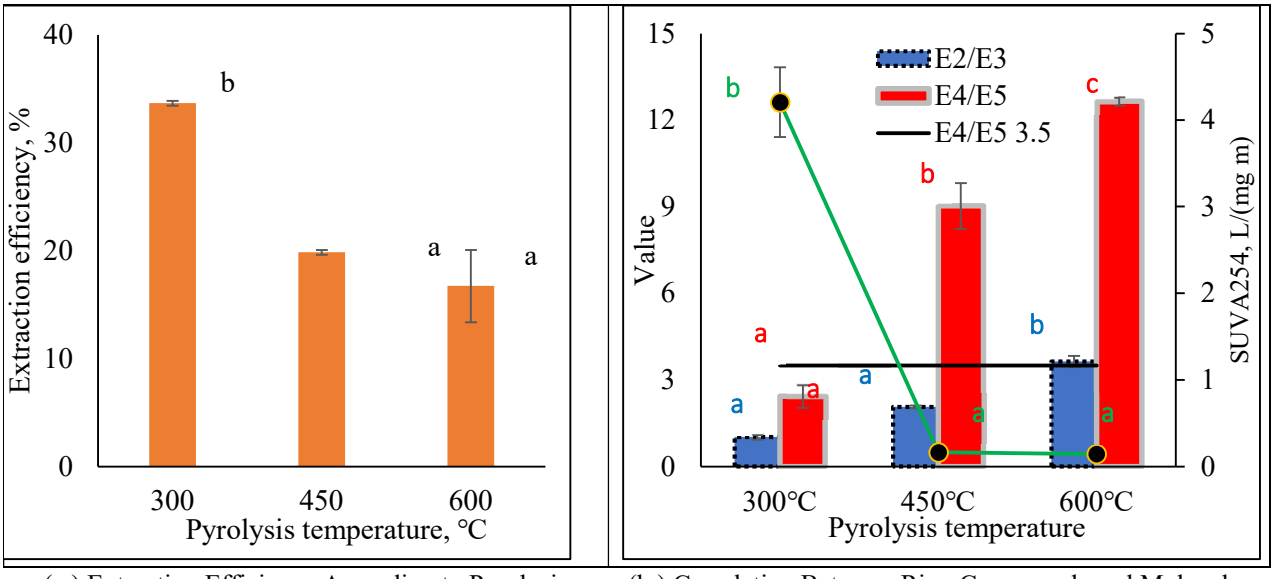
Table-1: Basic Composition of Biochar from Coffee Husks

Parameters	Coffee husk	Bio 300	Bio 450	Bio 600
Volatile matter content, %	80.6^{c}	61.0^{b}	44.5^{a}	44.5^{a}
SD	2.7	0.9	2.8	1.6
Fixed carbon content, %	11.2^{a}	28.2^{b}	39.7^{c}	38.3^{c}
SD	2.1	0.6	1.5	1.1
Ash content, %	8.2^{a}	10.7^{b}	15.8^{c}	17.2^{c}
SD	0.6	0.3	1.3	0.5

The letters $^{a, b, c}$ in the same row indicate statistically insignificant differences.

Effect of Pyrolysis Temperature

The effects of pyrolysis temperatures of biochar from coffee husks on the extracted DOC content under experimental conditions such as 1M KOH, 2h extraction time, 6000 rpm homogenization speed, and 100 g/L biochar dosage are shown in Fig.-1a. The results showed that when the pyrolysis temperature increased, the DOC extraction efficiency decreased, specifically with DOC extraction efficiency of 33.7; 19.6, and 16.7% respectively for biochar pyrolyzed at 300, 450, and 600°C. The obtained results were very high compared to the research results of Liu *et al.,* on rice straw ranging from 0.47 to 4.9%, which may be due to the raw materials, the alkali content used in the extraction as well, and the heating process during the biochar pyrolysis. A similar decrease in extraction efficiency was also found in the study of Liu *et al.,* which reported that the amount of DOC obtained decreased with increasing pyrolysis temperature from 300 to 600°C.[19]



(a.) Extraction Efficiency According to Pyrolysis Temperatures. The Letters ^{A,B} on the Graph Represent Significantly Different Values.

(b.) Correlation Between Ring Compounds and Molecular Weight According to Pyrolysis Temperature. The letters A and B in the Same Color Indicate Statistically Significant Differences

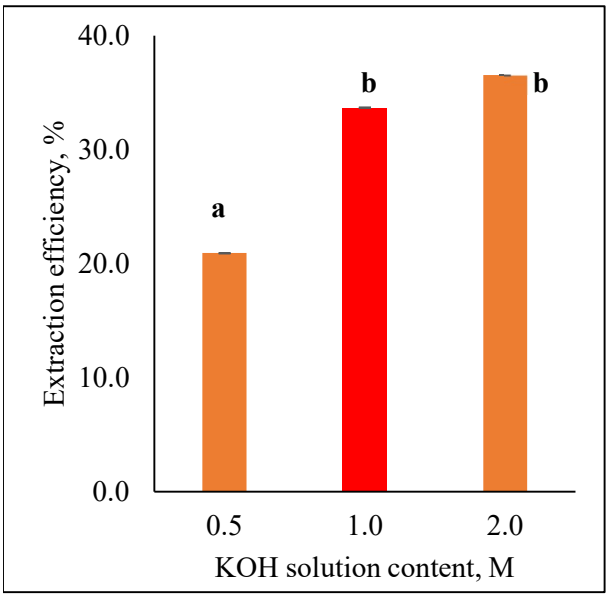
Fig.-1: Effect of Pyrolysis Temperature, Experimental Conditions such as KOH Content 1M, Homogenization Speed 6000 rpm, Extraction Time 2h, Biochar Dosage Used 100 g/L

When the pyrolysis temperature increased from 300 to 450°C, the DOC extraction efficiency decreased significantly. The efficiency changed insignificantly at pyrolysis temperatures of 450 and 600°C. This can be explained by the fact that increasing the pyrolysis temperature accelerated the carbonization process, which led to the continuous decomposition, condensation, cyclization, and polymerization of unstable organic compounds. A similar explanation was found in the study of Liu *et al.*[1] The results of determining the correlation between ring compounds and molecular weight through determining the E2/E3 ratio are presented in Fig.-1b. The results showed that the E2/E3 ratio increased with increasing pyrolysis temperature. Specifically, the E2/E3 ratio values were 1.0; 2.1, and 3.6 for Bio 300, Bio 450, and Bio 600 °C, respectively. A statistically significant difference occurred at pyrolysis temperatures of 450 and 600°C, while between 300 and 450°C there was no significant difference. The E2/E3 ratio in the study was lower than that in the study of Liu et al., specifically on biochar derived from rice straw (Brassica campestris L.) when pyrolyzed at 300 to 700°C.[19] This difference may be due to the different raw materials used in the study. The explanation is similar to that in the study of Liu *et al.*[1]. The E2/E3 ratio increases, Figure-1b, shows that the molecular size of the organic molecules in the extract solution decreases, or in other words, the molecular weight decreases [13]. Similar results were found in other studies[15,19] This can be explained by the fact that the pyrolysis reactions occur through various secondary processes such as decomposition, condensation, cyclization, and polymerization, leading to the formation of low molecular weight compounds. A similar explanation was also found in the study of Liu *et al.*[19] The calculation results of $SUVA_{254}$, Fig.-1b, showed that the SUVA254 value decreased by 4.2; 0.2, and 0.1 L/(mg m) respectively for Bio 300, Bio 450 and Bio 600. The $SUVA_{254}$ value is related to the aromaticity and hydrophobicity of DOC. The results showed that this level gradually decreases with increasing pyrolysis temperature, while the hydrophilicity increases. In particular, the aromaticity and hydrophobicity of Bio 300 are significantly higher than those of Bio 450 and Bio 600, which could be due to the presence of aliphatic compounds at low pyrolysis temperatures and they disappeared at higher pyrolysis temperatures when the aliphatic components evaporated or decomposed.[1] A similar decreasing trend of $SUVA_{254}$ was also found in the study of Liu et al, which used biochar derived from Brassica campestris L. at pyrolysis temperatures of 300, 500, and 700°C.[1] The hydrophobic component of DOC is of more interest in soil remediation applications because it can reduce the transport of heavy metals and dissolved organic pollutants while increasing the retention of mineral components.[1] When considering the E4/E5 ratio, Fig.-1b also showed that this ratio increases with increasing pyrolysis temperature, specifically the ratio increases by 2.4; 9.0, and 12.6 respectively for pyrolysis temperatures of 300, 450, and 600°C. This ratio increases significantly at pyrolysis temperatures. The increase in the E4/E5 ratio showed that the humidity, aromaticity, and molecular weight of humic acid-like substances are decreasing.[16] Only biochar pyrolyzed at 300°C had an E4/E5 value < 3.5, indicating that the DOC in this biochar extract was mainly humic acid-like substances.[16] Meanwhile, biochar pyrolyzed at 450 and 600°C had E4/E5 > 3.5 so the extract was mainly fulvic acid. Similar results were also found in the study of Liu et al., who found an increase in low molecular weight acids (protic organic acids) and neutral substances (low molecular weight alcohols, aldehydes, ketones, sugars, etc.) in biochar that were present at higher pyrolysis temperatures due to secondary pyrolysis reactions.[1] Based on the organic carbon extraction efficiency and the amount of humic acid-like substances obtained, Bio 300 was selected for the next experiments.

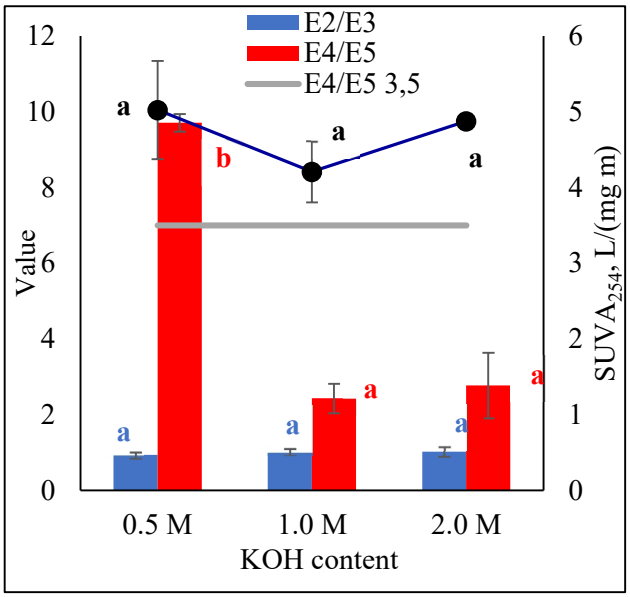
Effect of KOH Content

The results of the investigation on the influence of KOH content on the extraction process of organic carbon from Bio 300 under extraction conditions such as a homogenization speed of 6000 rpm, extraction time of 2 hours, and biochar dosage of 100 g/L were presented in Fig.-2a. The results showed that the DOC extraction efficiency increased with increasing KOH content. Specifically, the DOC extraction efficiency increased by 21.4; 33.7, and 34.5%, respectively, for KOH content of 0.5; 1.0, and 2.0 M. This can be explained by the fact that increasing the KOH content destroyed the binding force between organic acids and cations on the carbon surface, promoted the dissociation of carboxyl and phenyl groups, hydrolysis of weak covalent bonds (e.g., ether bonds and ester bonds) and cracking of internal chain bonds (e.g., aromatic rings and fat bonds)[4], increasing DOC content. [1] The increase was significant when the KOH content was from 0.5 to 1.0 M, but then insignificant when the KOH content was from 1 to 2 M. The reason may be that

the number of cations in the immobilized biochar sample was constant, so the DOC extraction efficiency did not increase significantly even though the amount of KOH still increased. Similar results and explanations were also found in the study of Cheng et al when using KOH solution.[4] Besides, it is also possible that increasing KOH content leads to the process of carboxyl destruction to produce CO_2, causing loss of DOC.[20] Figure-2b showed that the E2/E3 ratio increased by 0.9; 1.0 and 1.0 respectively with KOH content of 0.5; 1.0 and 2.0 M under extraction conditions. The results showed that when increasing the KOH concentration, the molecular weight of dissolved organic substances did not change significantly according to the Oneway ANOVA analysis. This showed that the KOH content did not significantly affect the aromaticity in the extraction solution.



(a.) DOC extraction efficiency according to KOH content. The letters [a,b] on the graph represent significantly different values.



(b.) Correlation between aromatic compounds and molecular weights according to KOH content. The letters [a,b] in the same color indicate statistically significant differences

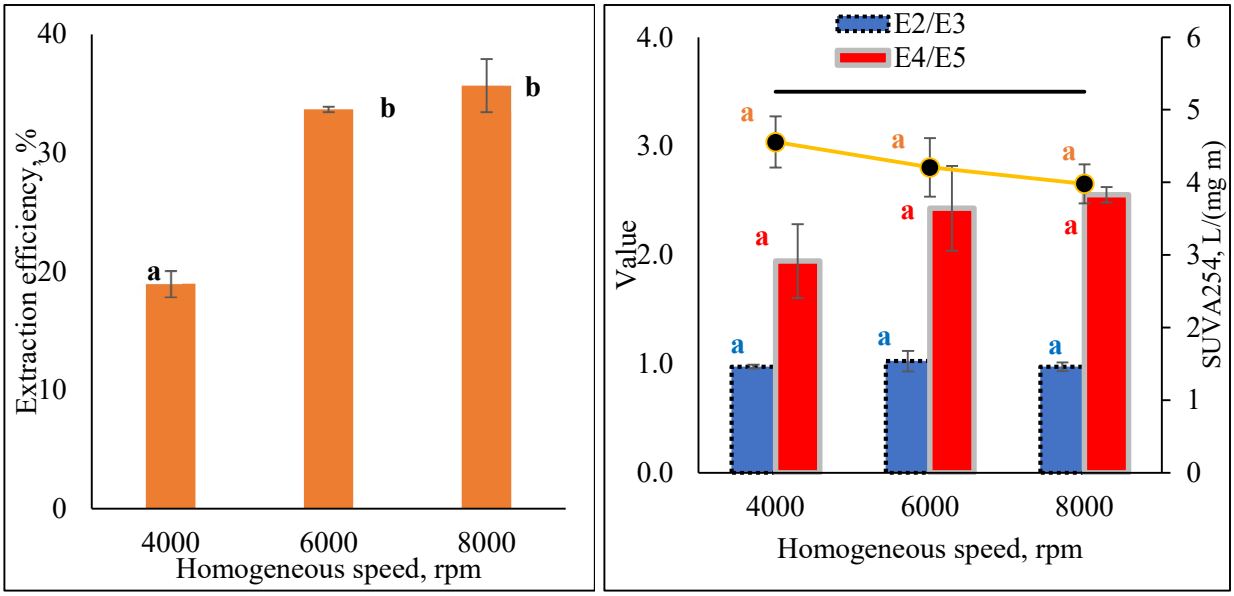
Fig.-2: Effect of KOH Content, Extraction Conditions Such as Bio 300, Homogenization Speed 6000 rpm, Extraction Time 2h, Biochar Dosage used 100g/L

The calculated results of SUVA254, Fig.-2b, were 5.0; 4.2, and 4.9 L/(mg m) for KOH concentrations of 0.5; 1.0, and 2.0 M, respectively. The SUVA254 values at 0.5M and 1.0M KOH concentrations were statistically significantly different, while between 1.0 and 2.0 M, insignificant. This could be explained by the fact that some soluble organic substances were decomposed and converted into insoluble substances.[21] The E4/E5 ratio decreased when the KOH solution content increased. Specifically, the ratios were 9.7; 2.4, and 2.8, respectively, corresponding to KOH content of 0.5; 1.0, and 2.0 M. The decrease was significant at KOH 0.5 and 1.0 M and insignificant at KOH 1.0 and 2.0 M. The results also showed that when the KOH solution content was 1.0 and 2.0 M, the extracted solution was mainly humic acids (E4/E5<3.5).[15] This can be explained by the increased presence of OH^-, which increased the dissociation of carboxyl and phenyl groups, and the cracking of ester bonds also released organic substances with larger molecular weight and more aromaticity from the biochar surface.[1] In the case of 0.5 M KOH with E4/E5 of 9.7 (>3.5), DOC contains many low molecular weight organic substances, which may be easily soluble organic substances. This may be due to not having enough alkalinity to dissolve organic substances with large molecular weights like humic acid. Based on the DOC extraction efficiency and the obtained humic acid-like substances ratio, Bio 300 and the KOH extraction solution content of 1.0 M were selected for the next experiments.

Homogenization Speed

Investigation of the effect of homogenization speed with conditions such as Bio 300, and KOH 1M showed that the extraction efficiency increased with increasing homogenization speed Fig.-3a. Specifically, the

DOC extraction efficiency increased by 19.0; 33.7, and 35.7% respectively at homogenization speeds of 4000, 6000, and 8000 rpm. The increase was statistically significant at speeds of 4000 and 6000, then increased insignificantly at 8000 rpm. Sargazi *et al.* also suggested that stirring speed has a positive effect on the extraction yield because equilibrium is achieved faster at higher stirring speeds.[22] The increase in DOC extraction efficiency may be due to the increase in the homogenization rate, the specific surface area, and the pore structure of the biochar surface increase, which leads to the fracture and deformation of weak chemical bonds on the biochar surface. Furthermore, the deprotonation of salts of humic acid-like compounds and alkyl structures also reduces the molecular weight and increases the content of oxygen-containing functional groups.[4] In addition, when the homogenization speed is slow, large biochar aggregates may form, causing the reaction to be incomplete and the colloidal particles cannot be separated from the biochar surface. Homogenization speed that is too fast may cause the particles formed to be too small, so they are likely to adhere to the biochar particles. A similar explanation was found in the study of Supraba *et al.* [23]



(a.) DOC extraction efficiency according to homogenization rate. The letters [a,b] on the graph represent significantly different values.

(b.) Correlation between aromatic compounds and molecular weights according to homogenization speed. The letters [a,b] in the same color indicate statistically significant differences

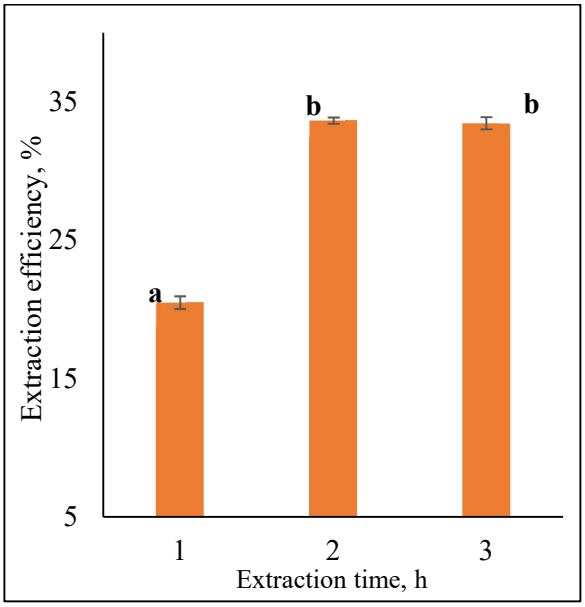
Fig.-3: Homogenization Speed (extraction conditions such as Bio 300, 1M KOH, extraction time 2h, biochar dosage used 100g/L)

The E2/E3 ratio did not change (~1.0) when increasing the homogenization speed at 4000, 6000, and 8000 rpm, Fig.-2b. The results showed that the homogenization speed did not affect the DOC composition and did not change the molecular size of organic matter. Similarly, when considering the E4/E5 ratio, Fig.-2b, it was also shown that there was no significant change when changing the homogenization speed. Specifically, the E4/E5 ratio was 1.9; 2.4, and 2.6 (<3.5) respectively. This result confirmed that the proportion of humic acid-like organic substances did not change when changing the homogenization speed. The calculated results of SUVA254, Fig.-2b, the values are 5.0; 2.4, and 2.6 L/(mg m) respectively for homogenization speeds of 4000, 6000, and 8000 rpm. However, this change is not statistically significant, in other words, the homogenization speed did not change the aromaticity and molecular weight of organic substances in the extract solution. Based on the calculation results of the ratios E2/E3, E4/E5, and SUVA254, it was confirmed that when the KOH content is large enough, the extracted solution is mainly organic substances with large molecular weight like humic acid. Increasing the homogenization speed did not significantly change the organic matter composition in the extracted solution. Similar observations were also found in the study of Jaing *et al.* that with a fixed alkali content and lignite dosage, the stirring speed did not change the composition of the humic acid obtained.[21] Based on the DOC extraction efficiency and

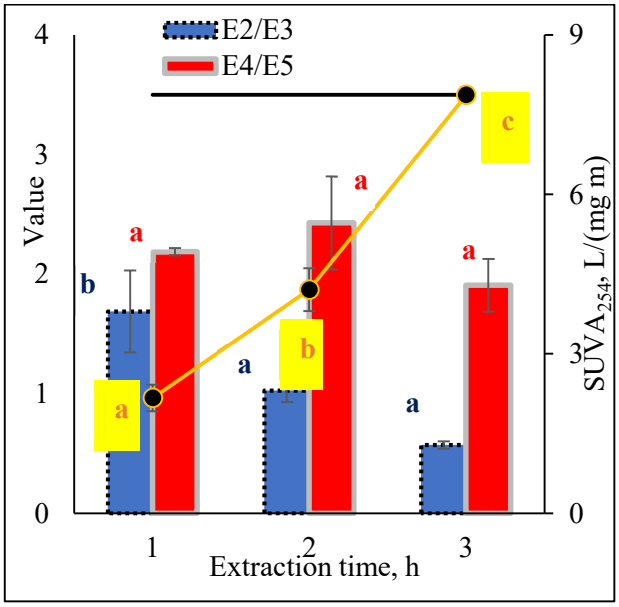
humic ratio obtained, taking into consideration the energy consumption, Bio 300, 1.0 M KOH, and homogenization speed 6000 rpm were selected for the following experiments.

Effect of Extraction Time

The results of the investigation of the effect of extraction time on DOC extraction efficiency under conditions such as Bio 300, KOH 1M, homogenization speed of 6000 rpm, and biochar dosage of 100 g/L were presented in Fig.-4a. Specifically, the DOC extraction efficiency was 20.5; 33.7, and 33.5% respectively for extraction times of 1, 2, and 3 hours. The results showed that the DOC extraction efficiency increased significantly with the extraction time from 1 hour to 2 hours. After that, the change was not significant when continuing to increase to 3 hours.



(a.) DOC extraction efficiency according to extraction time. The letters [a,b] on the graph represent significantly different values.



(b.) Correlation between aromatic compounds and molecular weight according to extraction time. The letters [a,b,c] in the same color indicate statistically significant differences

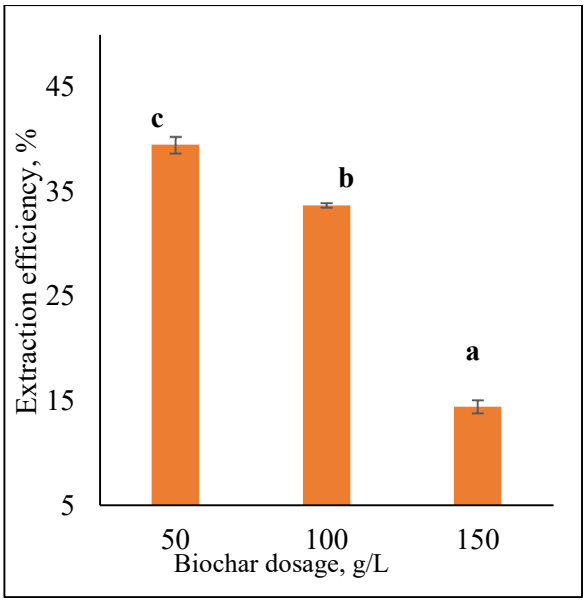
Fig.-3: Effect of Extraction Time (extraction conditions such as Bio 300, 1M KOH, homogenization speed 6000 rpm, biochar dosage used 100g/L)

The results can be explained by the fact that at the initial stage, at 1 h, due to the short time, the reaction has not yet reached a stable state. Only at 2 h, the extraction process reaches a higher and more stable efficiency. But when the time is continued to increase, the efficiency does not change significantly, this may mean that the extraction reaction has almost reached a saturated state. A similar explanation was also found in the study of Cheng *et al.* [4] Figure-4b shows the effect of extraction time on the variation of E2/E3 ratio with conditions such as Bio 300, KOH 1M, homogenization speed 6000 rpm, and biochar dosage 100 g/L. The results showed that the E2/E3 ratio decreased by 1.7; 1.0 and 0.6 respectively with extraction times of 1, 2, and 3 hours. Soluble organic substances with large molecular weight such as humic acid-like organic substances are more easily dissolved (participate in neutralization reaction). However, within 1 hour, the amount of these organic substances has not reached saturation. Only when the extraction time is extended to 2 hours, this is a sufficient time for the extraction process, then these compounds have increased statistically significantly. However, when the extraction time continues to increase, the organic composition does not change significantly. This can be explained by the fact that the dissolution process of organic substances with large molecular weight still occurs, along with the hydrolysis reactions that break the carbon chain to form organic substances with low molecular weight.[20] The calculated results of $SUVA_{254}$ were presented in Fig.-4b, this value increased by 2.2; 4.2, and 7.9 L/(mg m) respectively for extraction times of 1, 2, and 3h. One-way ANOVA analysis showed that $SUVA_{254}$ increased significantly at each selected time point in the experiment. $SUVA_{254}$ represents the aromaticity and hydrophobicity of the extract

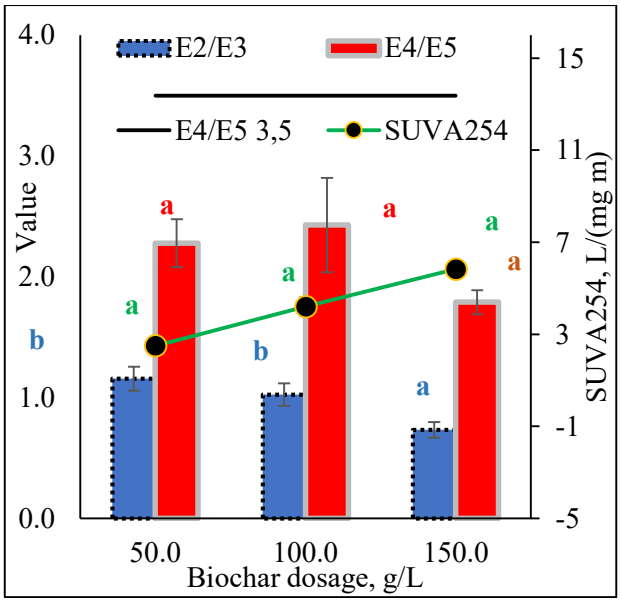
solution, the increase showed that the aromaticity and hydrophobicity increase with the extension of extraction time. The E4/E5 ratio did not change in a clear trend when the extraction time increased, Fig.-4b. Specifically, the E4/E5 ratio was 2.2; 2.4, and 1.9 (<3.5) for extraction times of 1, 2, and 3 hours, respectively. The ratio change was not statistically significant at the surveyed periods. The results showed that the extracted solution was mainly organic substances similar to humic acid.[15] The results showed that extraction time did not affect the composition of dissolved organic matter in the extraction solution. Based on the DOC extraction efficiency and the obtained humic ratio, Bio 300 and the 1M KOH 1.0 M, homogenization speed 6000 rpm, and extraction time 2h were selected for the following experiments.

Effect of Biochar Dosage

Figure-5a specifically presents the DOC extraction efficiency according to the biochar dosage used under extraction conditions including Bio 300, KOH 1M, homogenization speed 6000 rpm, and extraction time 2h. Specifically, the extraction efficiency decreased by 39.5; 33.7 and 14.4% respectively for biochar dosages of 50, 100, and 150 g/L. However, when calculated based on the DOC content in the extraction solution, the biochar dose of 100 g/L had the highest DOC content (33.2 g/L) compared to the biochar doses of 50 g/L (19.7 g/L) and 150 g/L (21.6 g/L). A similar optimum dosage was also found in the study of Rashid et al. when coal was extracted with a KOH solution.[24] This can be explained by the fact that when the biochar dosage is increased, the DOC content in the extraction solution increases to a saturation level. Then, if the biochar dosage continues to increase, the DOC does not increase further or even decrease due to the combination of biochar particles, reducing the contact area and reducing the extraction capacity.[24]



(a.) DOC extraction efficiency according to biochar dosage. The letters [a,b, and c] on the graph represent significantly different values.



(b.) Correlation between aromatic compounds and molecular weight according to biochar dosage. The letters [a,b] in the same color indicate statistically significant differences

Fig.-4 Effect of Biochar Dosage, (extraction conditions such as Bio 300, KOH 1M, homogenization rate 6000 rpm, extraction time 2h)

The results of calculating the E2/E3 ratio, Fig.-5b, showed that the E2/E3 ratio tended to decrease. Specifically, the ratios were 1.2; 1.0, and 0.7, respectively, for biochar doses of 50, 100, and 150 g/L. Analysis by ANOVA on SPSS 23 showed that this ratio decreased without statistical significance at biochar doses of 50 and 100 g/L, but it decreased significantly at doses of 150 g/L. The analysis results showed that the molecular size of organic molecules in the extraction solution increased, or in other words, the molecular weight increased. This can be explained that when the extraction process is not saturated, organic substances such as humic acid will dissolve first.[1] Figure-5b shows that SUVA254 increased with increasing biochar dosage. Specifically, SUVA254 increased by 2.5; 4.2, and 5.8 L/(mg m) respectively for biochar dosages

of 50, 100, and 150 g/L. The results confirmed that the qualitative calculation based on the E2/E3 ratio was accurate. The E4/E5 ratio, Fig.-5b, showed a non-significant change ranging from 1.8 to 2.4. The results confirmed that the biochar dosage used did not affect the proportion of humic acid-like organic matter in the DOC composition. Based on the DOC extraction efficiency and the obtained humic ratio, Bio 300, 1.0 M KOH, homogenization speed 6000 rpm, extraction time 2h, and biochar dosage 100 g/L were selected for the following experiments.

CONCLUSION

The aim was to determine the extraction parameters of biochar derived from coffee husks using KOH based on the extraction efficiency of DOC, and the contribution of DOC components with humic acid-like structures with high molecular weight. The results of the study on the optimal parameters for the DOC extraction process included biochar pyrolyzed at 300℃, KOH content 1M, homogenization speed 6000 rpm, extraction time 2 h, and biochar dosage used 100 g/L for extraction efficiency 33.7%, SUVA 4.2 L/(mg m). The study not only determined the optimal operating parameters for DOC extraction from coffee husk-derived biochar but also had the potential to maximize the benefits of biochar in agriculture (soil improvement and production of liquid organic fertilizers).

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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