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Optimization of the Carbonization Parameter of Exhausted Coffee Husk (ECH) as Biochar for Pb and Cu Removal Based on Energy Consumption

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ABSTRACT

Recent studies on agricultural waste as a potential precursor of biochar for heavy metals removal from aqueous solution had not considered exhausted coffee husk (ECH) as the potential one. It is well-known that the carbonization process influences the removal performance of biochar, particularly removal efficiency (RE). However, previous studies rarely considered the energy consumption during the carbonization process. The major objective of this study is to investigate the optimum carbonization parameter on ECH biochar for removal of ion Pb and Cu from economic stand point. The ECH biochar was produced at the different heating temperature (300 – 600 °C) and heating time (30 – 120 minutes). In regard to specific cost of bio-sorption, the results showed that 500 °C was the optimum heating temperature of ECH biochar for the Pb removal, while 600°C was the optimum one for the Cu removal. Furthermore, the heating time experimental outcomes suggested that the optimum heating time were 30 minutes for Pb removal and 120 minutes done Cu removal.

1. INTRODUCTION

Population growth and anthropogenic activity benefit the rise of industrialization yet are also resulting in several detrimental consequences that are directly attributed to the pervasiveness of pollutants in the ecosystem, particularly in the hydrosphere (Inamuddin, 2019). Water resource contamination has been a contentious issue that attracts worldwide concerns due to its long-term or even deadly consequences to living organisms (Schwarzenbach *et al.*, 2006). Water bodies has been increasingly contaminated with industrial effluents including heavy metal ions such as lead (II) and copper (II) (Qasem *et al.*, 2021).

The accumulation of lead ion (Pb^{2+}) and copper ion (Cu^{2+}) in wastewater has become a great challenge in developing countries, such as Indonesia (Inglezakis *et al.*, 2003). In the country, effluents containing the ions are often indiscriminately discharged into water bodies or on land. The accumulation of the ions in water bodies are hazardous and leads to fatal health challenges if the concentration is higher than the given standards (Duruibe & Egwurugwu, 2007; Salem *et al*., 2000). Furthermore, these metal ions are not ecologically degradable and yet undergo an ecological cycle main pathways to nearby agricultural soil and groundwater (Ezigbo *et al*., 2016; Phuengphai *et al*., 2021; Smith *et al*., 1996). Consequently, residues of the heavy metals inevitably pollute water bodies in the agricultural environment.

A series of post-combustion technologies have been investigated for heavy metals removal from water, including adsorption of Pb^{2+} and Cu^{2+} (Salim *et al*., 2016; Qasem *et al*., 2021). It has been considered as a cost-efficient method and furthermore its removal efficiency in the wastewater treatment have been the driving force behind its extensive usage (Abbas *et al*., 2014; Sharif *et al*., 2019; Tan *et al*., 2015). However, the production of commercially available activated carbon does entail several challenges; one of them being the high manufacturing costs (Michalak *et al*., 2013; Tan *et al*., 2015). The precursor material used for the production of AC such as coal and lignocellulosic material from biomass are expensive to procure and often need to be imported. There has been a growing interest wherein the feasibility of using alternative lignocellulosic biomass from agricultural activities such as coffee residues (Ayalew & Aragaw, 2020; Gonçalves *et al*., 2013).

The first by-product generated during coffee processing is cascara (Iriondo-Dehond et al., 2020). The definition and composition of this by-product depends on the type of processing employed (Mussatto et al., 2011). Coffee cascara obtained from the dry method comprises nearly 45% of the coffee cherry (del Castillo et al., 2019). Every 10 ton of coffee harvested generates nearly 5,7 ton of coffee bean while the rest 4,3 ton will become cascara that ends up as a waste. In Indonesia, it was estimated that approximately 634,8 ton of coffee was produced in 2021 (Global Agricultural Information Network, 2022). Thus, nearly 285,66 ton of cascara is potentially produced annually in Indonesia. To increase the eco-sustainability of the coffee industry, by-products should be exploited before they become waste. Recently, cascara has been processed into a diffusion drink known as cascara tea (Klingel et al., 2020). However, this coffee-by product processing method is still resulting solid cascara waste in a form of exhausted coffee husk (ECH).

As a result, among potential coffee residue types, ECH, a by-product of cascara tea production has shown a promise due to its comparatively easier availability. In addition to the mentioned challenge, for adsorption technology, the utilization of adsorbent is still restricted by high energy consumption during the combustion (Calvo-Muñoz *et al*., 2016). Recently, some modifications on the technologies have been applied in the demonstration research project to obtain an effective removal of heavy metal ions yet economical. Previously, researches had been done on of coffee husk (CH) as a potential agricultural waste precursor for bio-sorbent (Ayalew & Aragaw, 2020; Rodiguez *et al*., 2018; Oliveira *et al*., 2008).

However, to our best knowledge, studies of ECH as bio-sorbents for removal of the heavy metal ions from aqueous solutions has not been initiated in Indonesia. This study had attempted to investigate economical technique of utilization of biochar from ECH. Various operational parameters have been applied, namely heating temperature and heating time. Finally, the analysis moves to the evaluation of process costs. Specific costs and the ECH biochar value related of its best performance process conditions were calculated. Proper yet economical operating conditions, are indeed of interest not only from an environmental point of view, namely circular economy and zero-waste approaches, but also from an economic standpoint.

2. MATERIAL AND METHODS

2.1. Materials

The ECH was collected from the local cascara processing unit, PT. AGAVI, in West Java, Indonesia. The ECH from the infusion process of cascara tea was then dried under the sun for 15 hours. Meanwhile, Pb (II) and Cu (II) working solutions (20-100 mg/L) were prepared by diluting the stock solutions (1000 mg/L) of $Pb(NO_3)_2$ and $Cu(NO_3)_2$ with ultrapure water prior to the batch adsorption experiments. All chemical agents were of analytical grade. $Pb(NO_3)_2$ and $Cu(NO_3)_2$ stock solutions, phosphoric acid (H_3PO_4), potassium hydroxide (KOH), and zinc chloride ($ZnCl_2$), were purchased from Merck, KGaA, Darmstadt, Germany.

2.2. Methods

2.2.1. Standard solutions (Pb^{2+} and Cu^{2+}) preparation

The known Pb (II) and Cu (II) standard solutions (0, 0,5, 1, 2, 5 mg/L) were prepared by diluting the $Pb(NO_3)_2$ and $Cu(NO_3)_2$ stock solution with ultrapure water. Their concentrations were measured by Shimadzu AA-7000 atomic absorption spectrophotometer (AAS) (Shimadzu, Japan). Linear calibration curves were plotted from absorbance values versus the respective concentrations of Pb (II) solutions and Cu (II) solutions (Figure 1).

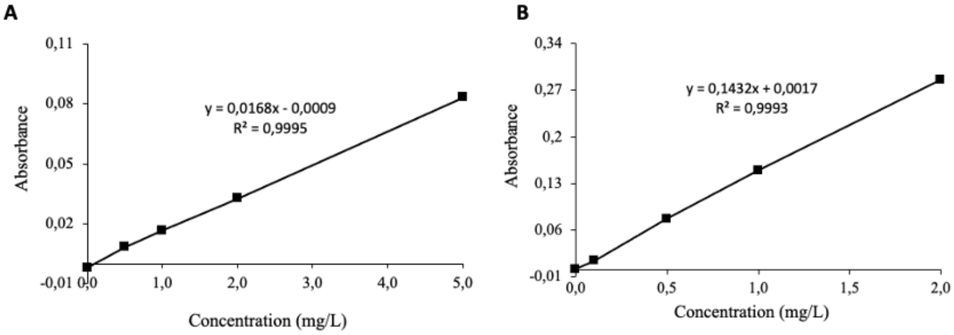


Figure 1. Calibration Curve of Pb (a) and Cu (b)

2.2.2. Carbonization preparations

A series of single-factor experiments were conducted to investigate the specific costs of biochar utilization process. For this purpose, energy consumption of each process with different heating temperatures and heating times aligned with its removal efficiency were investigated. Various heating temperatures (300 – 600 °C) and heating time (15 – 120 min) were applied during the carbonization process, respectively. One parameter was applied variedly, while the other parameters were remained constant. In addition, the gradient was remained constant of 5 (°C/min) for all the carbonization process. The gradient time was the rate of increasing temperature from room temperature to reach the heating temperature. Furthermore, the 30 g of dried ECH was carbonized with Muffle Furnace (Nabertherm B180) A ceramic crucible bowl in a muffle furnace was used for the muffle furnace. During the process, the ceramic crucible bowl was wrapped with aluminum foil to isolate the oxygen. The activated powder was kept in a plastic bag placed in a desiccator for the subsequent experiment and adsorbent characteristic.

Table 1. Experimental Design

No.	Experiment	Temperature (°C)	Carbonisation Time (min)	Total Process Time (min)
1.	Different heating temperature	300	60	120
2.		400		140
3		500		160
4.		600		180
5.	Different heating time	500	30	130
6.			60	160
7.			120	220

2.2.3. Carbonization Yield

Efficiency of the carbonization is expressed as the yield (*Y*) of biochar in gross terms is expressed as a percentage of the ECH charged or used-up to produce it. Yield of each carbonization with the different carbonization operational parameter was calculated using the following equation:

$$Y\ (\%) = \frac{W}{W_0}\ x\ 100\% \qquad (1)$$

where W is the weight of the prepared biochar after the carbonization and W_o is the weight of the raw ECH before carbonisation.

2.2.4. Bio-sorption removal efficiency and capacity experiments

The bio-sorption performance of all prepared ECH were conducted in batch experiments. The experiments were performed in 250 mL Erlenmeyer flask containing 100 mL of the heavy metal solutions with initial concentration of 20 mgL^{-1}. The dosage of ECH biochar added into the flasks with the solution was 1 g. The flasks were shaken with orbital incubator shaker (IKA KS 3000 i) at a speed of 50 rpm/min and contact time of 40 min at 295 K. At the end of each experiment, the supernatant solution was withdrawn before filtered with Whatman filter paper. The filtered solutions were diluted prior to the heavy metals concentration measurement with AAS. The amount of Pb^{2+} and Cu^{2+} absorbed each was expressed as removal efficiency (RE%). The RE and adsorption capacity were determined by using the following Equations (2) and (3), respectively (Zhou *et al.*, 2019).

$$RE\ (\%) = \frac{C_o - C_t}{C_o} * 100\% \qquad (2)$$

$$q_t = \frac{(C_o - C_t)\,V}{m} \qquad (3)$$

where C_o is the initial concentration of Cu^{2+} (mg/L), C_t is the final concentration of Cu^{2+} after bio-sorption (mg/L), q_t is the adsorption capacity (mg/g), V is the solution volume of Cu^{2+} (mL), and m is the adsorbent dosage (g).

2.2.5. Energy Consumption and Production Cost

The energy consumed during carbonization process of each experiment, production cost and specific energy bio-sorption cost were calculated by using the following Equations (4), (5) and (6), respectively:

$$E\ (kWh) = \frac{Power\ x\ carbonisation\ time}{60} \qquad (4)$$

where Power is assumed as 3,6 kW and carbonization time is in min. Whereas, production cost (*PC*) and specific energy biosorption cost (*SEBC*) are calculated as the following.

$$PC\ (Rp/g) = \frac{Energy\ consumption\ (kWh)\ x\ Electricity\ cost\ (Rp/kWh)}{Biochar\ produced\ (g)} \qquad (5)$$

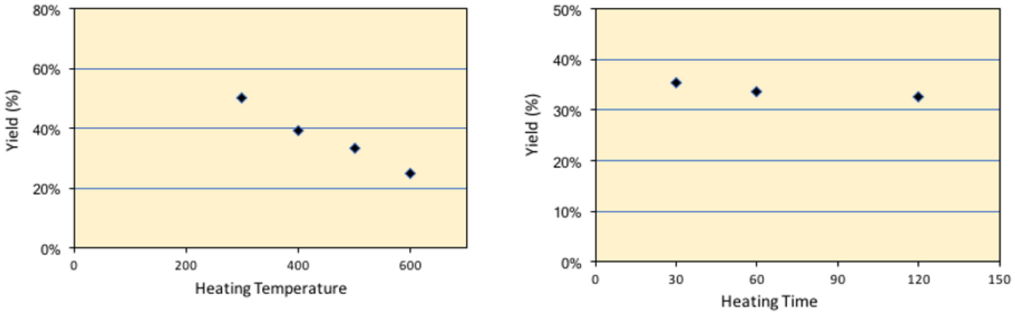
$$SEBC(Rp/mg) = \frac{Production\ cost\ (Rp/g)}{adsorption\ capacity\ (mg/g)} \qquad (6)$$

where, the electricity cost is 1444,7 (Rp/kWh) (PLN, n.d.).

3. RESULTS AND DISCUSSION

3.1. Carbonization Yield

The effect of temperature on the yield of biochar produced with different heating parameters were summarized in Figure 2a. It is remarkable that the final yield in percentage presented different tendencies with different carbonization parameters. In fact, the final yields of the biochar were ranged between 52% and 25% for temperatures between 300°C and 600°C, respectively (Figure 2a).



(a) (b)

Figure 2. Yield of ECH carbonization at different heating temperatures (a) and heating time (b)

The increasing in carbonization temperature generally lead to a decreasing yield. It can be observed that the rate of lost were increased with an increasing of heating temperature. These yields trends were in accord with the report in previous studies investigating the carbonization of biomass with different heating temperature (Huang *et al*., 2021; Titiladunayo *et al*., 2012). The increase in carbonization temperature and time generally lead to an increasing in heat transfer to the inner biomass material which increases the conversion rate of organic material. Hence, from Figure 2b it was seen that heating of 500°C at different heating time of 30, 60 and 120 minutes, led to slightly different weight loss rate. The longer heating time at the applied temperature led to more weight loss of the biomass. Therefore, it is expected that the yield continues to decrease as temperature and time of activation increases.

3.2. Energy Consumption per Biochar Produced

The decreased yield along with the increasing temperature were expected to affect the energy consumption and production cost of biochar production. Table 2 presented the production cost and specific production cost per gram of biochar from ECH produced with the varied heating temperature.

Table 2. The production cost and specific production cost of ECH biochar at various heating temperature

Cost Parameter	**Temperature**			
	300°C	**400°C**	**500°C**	**600°C**
Furnace power (kWatt)	3,6			
Electricity Cost (Rp/kWh)	1444,7			
Process Time (minute)*	120	140	160	180
Power consumption (Kwh)	7,2	8,4	9,6	10,8
Production Cost (Rp)	10402	12136	13869	15603
Biochar Produced (g)	15,1	11,8	10,1	7,4
Specific Production Cost (Rp/g)	691	1032	1378	2097

It was clearly seen from the table that the increasing of the heating temperature expectedly led to increasing production cost of the biochar. This was due to the higher temperature requires longer time to reach the desired constant temperature, therefore, it results in an increasing of power consumption. Furthermore, as the increasing temperature also had reduced the yield of the biochar production, therefore the specific production cost of each gram of biochar was also reached the highest at the highest temperature applied in the experiments.

The increasing trend was also seen with the investigation of the heating time effect. Table 3 was displaying the production cost and specific production cost per gram of biochar from ECH produced with the various heating time. Expectedly, the heating time resulting in power consumption during the process, which eventually resulted in higher production cost. Moreover, aligned with the increasing of heating temperature, with the decreasing effect on the yield, hence the longer heating time also resulted in higher production cost.

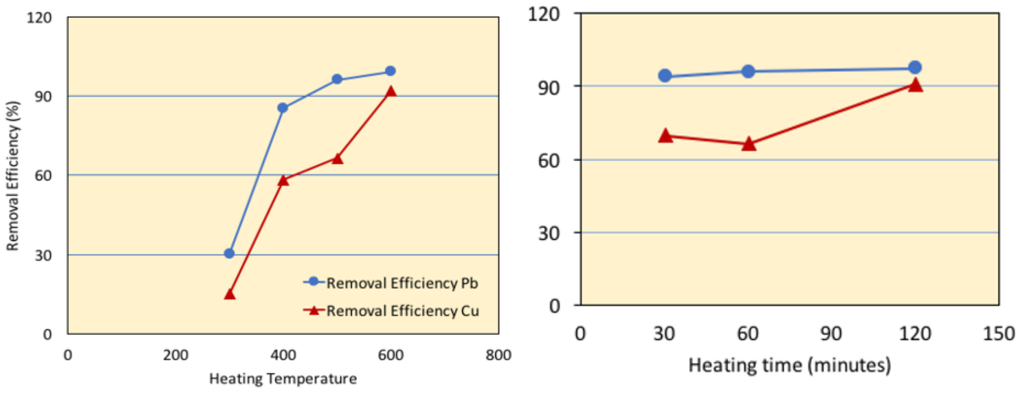
Table 3. The production cost and specific production cost of ECH biochar at various heating time

Cost Parameter	**Heating Time (minutes)**		
	30	**60**	**120**
Furnace Power (kWatt)	3,6		
Electricity Cost (Rp/kWh)	1444,7		
Process Time (minute)*	130	160	220
Power Consumption (Kwh)	7,8	9,6	13,2
Production Cost	11269	13869	19070
Biochar Produced (g)	15,1	11,8	10,1
Specific Production Cost (Rp/g)	7489	1179	1895

3.3. Optimum Parameter

Regarding to economic stand point, the optimum parameters for ECH combustion in the experiments were evaluated based on the removal efficiency (RE) (%) and specific cost for bio-sorption of the heavy metal. Figure 3 displayed the RE of the heavy metals at the different heating temperature and the different heating time.

From Figure 3a, it was clearly seen that REs obtained were increased with the increasing of heating temperature on the carbonization process of ECH. Noteworthy, the biochar achieved higher removal on ion Pb^{2+} than in Cu^{2+}. The trend was also found in the previous study by Salim *et al.* (2016). Even though toxic heavy metals are generally around the same pH level, which is acidic, however Pb has shown an initial pH of 2.2, while Cu showed an initial pH of 2.3. The slightly difference in the pH of the heavy metals could be the cause of the removal of Pb was more favorable than Cu (Phuengphai *et al*., 2021). The similar result was also found at the different heating time from Figure 3b.



(a) (b)

Figure 3. The removal efficiency (RE) (%) of ECH biochar for Pb2+ and Cu2+ removal at (a) different heating temperature and (b)different heating time of carbonization

Interestingly, from Figure 3a, the increasing temperature from 500 °C to 600 °C for biochar carbonization resulted in a significant increasing of Cu removal from 66,4 % to 92%. However, for Pb removal, the biochar from 500 °C carbonization could remove 96,1% of the ion Pb. Furthermore, the increasing temperature to 600 °C resulted in the RE increase was only by 3,2%. Meanwhile, the increasing trend was also seen with the increasing of heating time (Figure 3b). This trend is in accordance with the study done by Wu *et al.* (2018). The study showed that removal rate of the contaminant from the solution increased gradually as the increasing of carbonization temperature from 300 °C. In addition, the removal rate was also found increased in the study with the extended pf carbonization time. Furthermore, the results also presented that the pore size of changed with the prolonged carbonization time. Hence, it the prolonged pore size with the increasing heating temperature and time could have led to the increasing of RE on he biosoprtion process in the experimental studies.

3.3.1.Optimum Heating Temperature

Eventually, the increasing carbonization temperature also led to increasing of adsorption capacity by the biochar. However, from economic standpoint, the process that utilizes a minimal amount of electrical energy and cost would be recommended as the optimum operational parameters. Hence, the specific cost of bio-sorption for each heating temperature was calculated. Table 4 displayed the adsorption capacity and specific cost of bio-sorption for all the heating temperatures applied on the heavy metals removal.

It was clearly seen from Table 4 that generally the increasing heating temperature spent more specific cost than that of the lower temperature. For the Pb ion, regarding to specific bio-sorption cost, the lowest cost was at temperature of 400 °C. However, at that temperature, the RE achieved was still lower that 90%. The RE for the ion could be achieved above 90% when the biochar was heated at temperature of 500 °C and 600 °C.

Table 4. The adsorption capacity and specific cost of bio-sorption for all the heating temperature

Biosorption Parameter	Heating Temperature (°C)			
	300	400	500	600
Adsorption Capacity Pb (mg/g)	0,6	1,7	1,9	2,0
Specific cost of biosorption Pb (Rp/mg)	1151,5	606,8	717,8	1053,7
Adsorption Capacity Cu (mg/g)	0,3	1,2	1,3	1,8
Specific cost of biosorption Cu (Rp/mg)	2302,9	859,6	1060,2	1164,9

Furthermore, the increasing temperature to 600 °C impacted on increasing specific energy cost by 46,8% but the increasing of RE obtained was only by 3,2%. Hence, concerning the specific energy cost of each temperature and the RE obtained, carbonization temperature at 500 °C was suggested as the optimum carbonization heating temperature of ECH biochar for Pb removal. Meanwhile, for the Cu ion removal, the biochar from 600 °C achieved 92% while the biochar from the other three conditions were could not achieve higher than 70%. In addition, increasing the temperature from 500 °C to 600 °C only increase the specific energy cost by 9,8% with an increasing of RE by 38,5%. Hence, in particular for Cu removal, the ECH biochar was suggested to be carbonized at temperature of 600 °C.

3.3.2. Optimum Heating Time

In addition to heating temperature, the other parameter that affect specific cost is the optimum heating time. Table 5 presented the adsorption capacity and specific cost of bio-sorption for the heavy metals. Similar to the trend from the heating temperature experiments, the increasing heating time generally resulted in the increasing of specific energy consumption for both heavy metals.

Table 5. The adsorption capacity and cost of bio-sorption at different heating time

Biosorption Parameter	Heating Time (minutes)		
	30	60	120
Adsorption Capacity Pb (mg/g)	1,9	1,9	2,1
Specific cost of bio-sorption Pb (Rp/mg)	400,2	614,0	902,4
Adsorption Capacity Cu (mg/g)	1,4	1,3	1,8
Specific cost of bio-sorption Cu (Rp/mg)	534,6	906,9	1052,8

However, it was observed from Figure 2b that all the REs from the experiment were higher than 90% for all different heating time applied for ion Pb. Longer heating time from 30 minutes to 60 minutes and 120 minutes were only increasing the RE by 2,3% and 3,8%. Yet, the specific bio-sorption cost resulted in increasing by 53,4% and 125,5%. Hence, regarding to the previously mentioned points, 30 minutes was suggested as the optimum carbonization time of ECH biochar from this experiment.

On the contrary for Cu removal, longer carbonization time of 120 minutes resulting in significant increase of RE. The heating time at 30 and 60 minutes were only resulting in RE up to approximately 70%, while the 120 minutes of carbonization achieved in 91%. With regard to specific energy consumption, the increasing from 60 minutes to 120 minutes resulting in increasing cost of 16%. Therefore, in particular for ion Cu removal, 120 minutes of carbonization time was economically recommended.

4. CONCLUSION

The study explored specific cost of bio-sorption of ECH on Cu and Pb ions with different carbonization parameters applied, namely heating temperature and heating time. In addition to energy consumption, the yield, removal efficiency (RE), and adsorption capacity were also considered during the biochar carbonization process with the different operational parameters. The specific cost bio-sorption were investigated by evaluating the energy consumed per biochar produced and removal efficiency for both ions. The outcomes showed that generally the increasing of heating temperature and heating time resulted in decreasing the yield of ECH biochar. On the contrary, the RE, adsorption capacity and energy consumption were increased by the increasing of the temperature and time. The outcomes showed that 500 °C was the economically optimum heating temperature of biochar from ECH for ion Pb removal from aqueous solution while for ion Cu removal was 600°C. Furthermore, the heating time of 30 minutes was chosen as the economically efficient heating time for ion Pb removal while 120 minutes was strongly suggested for removal of ion Cu.

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