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Application of Agro-industrial Solid Waste as Biochar for Iron (II) Removal from Aqueous Solution

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ABSTRACT

In recent years, various industrial activities have introduced a high concentration of iron in the waterbody which causes serious problem to environment. This paper proposed the application of Exhausted Coffee Husk (ECH) as the biosorbent (BS) for removing iron (Fe) (II) in the aqueous solution. The ECH was carbonized into biochar before performing biosorption of the heavy metal ion. The effect of carbonization temperature, time and rate on the performance of the ECH biochar for removing Fe (II) were evaluated. The percentage of removal efficiency (RE) and the capacity of biosorption (mg/g) were considered as the determining parameters. The pyrolysis temperature was varied in a range of 200-600 °C with 50 °C of interval, while the time was in between 1h – 3h with a n interval of 0.5 h, and the temperature gradient of 5 – 25°C/min. The results showed that the temperature had a significant effect on the properties of the ECH biochar as BS for Fe (II). The temperature of 550 °C, at 1.5 h of time and 25 °C/min was chosen as the suggested carbonization temperature of biochar from ECH for biosorption of Fe (II).

1. INTRODUCTION

Heavy metals in the environment can be found in water, atmosphere and sediments (Rhaman *et al*., 2020). It has been reported that the concentration of heavy metals to be elevated in the wastewater generated by various anthropogenic causes, for instance stainless steel welding, construction, structure demolition, lead piping and fittings fertilizer production (Ebrahimi *et al*., 2019), pesticide production (Liu *et al*., 2019) and the intensification of agriculture output (Rhaman *et al*., 2020). Among the heavy metals on the earth, Iron (Fe) is the most common metal as it is essential nutrient for enzymes and proteins in humans, plants and algae (Zhang *et al*., 2014). However, it can be toxic at high levels (Jaishankar *et al*., 2014). The presence of the excessive Fe in the upper layer of the soil affects the behavior of the present phosphorus in the soil, which ceases its availability to plants and soil microorganisms. The phenomena will result in a degradation of arable land and significant economic losses (Corral-Bobadilla *et al*., 2021).

To this date, various technology processes have been investigated for treating water from Fe ions contamination like chemical precipitation, electrocoagulation, electro-dialysis, ultrafiltration (Fu & Wang, 2011; Dai *et al*., 2018; Qasem *et al*., 2021). However, the processes have their own inherent limitations such as sensitive operating conditions and costly. Adsorption is another powerful technology process for water purification. Recently, the high cost issue of carbon that restricts its application has been resolved by utilization of agro industrial and agricultural biomass wastes as biosorbents (BS). Various types of the biomass wastes have been used as BS of Fe ion from water including palm oil (Khosravihaftkhany *et al*., 2013) coffee and tea powder (Elsherif *et al*., 2018), carrot (Ebrahimi *et al*., 2019), olive stone (Corral-Bobadilla *et al*., 2021), rice husk ash (Hosseinzadeh & Mohammadi, 2016) and orange peel (Adebayo *et al*., 2016).

The main objective of this study is to propose the solution for treating a highly contaminated water with Fe ion by readily produced biochar. However, the selection of a suitable BS for a particular metal requires an experimental research. Another prospective agro industrial biomass waste that can be utilized as BS is exhausted coffee husk (ECH) from the production of cascara drink. The use of biochar from ECH still remains rare while the coffee constitutes one of the food industry's most polluting waste product (GAIN, 2022). The use of the biomaterial may affect the role of agriculture in the economy as it applies the concept of agricultural circular economy (Yaashikaa *et al*., 2020). The biomass material had studied previously as BS for lead (Pb) and copper (Cu) in a form of biochar. To our best knowledge, the effectivity of ECH as BS for Fe removal from water has not been studied.

There are two main factors that influences the development of biochar from carbon based biomass namely, nature of biomass and carbonization approach. Carbonization process plays an important role in favoring generation of porosity and active sites that trap the pollutants from water (Prasannamedha *et al*., 2021). It has been reported that carbonization temperature, time and rate influence the performance of biosorbent for particular metal from water (Zhou *et al*., 2019; Puari *et al*., 2022; Rusnam *et al*., 2022) The effect of carbonization parameters of utilizing biosorbent from ECH has become a subject of the study to provide an economical and environmental friendly method for utilizing an affordable biosorbent for Fe ion removal from water.

2. METHODOLOGY

2.1. Standard Solution

To prepare the heavy metal solution of Fe, standard stock solution $Fe(NO_3)_2$ (1000 mg/L) (Merck) was diluted with sterilized distilled water in 100 mL flask. The dilution number of the stock solution was varied to generate the standard solution with different concentrations. The standard solutions were used to generate the standard curve of the heavy metal analysis with Atomic Absorption Spectrophotometer (AAS) (AA 7000 Shimadzu, Japan). The standard curve was displayed in Figure 1.

2.2. Biochar Preparation

Exhausted coffee husk (ECH) was collected from cascara infused drink company, PT. AGAVI, West Java, Indonesia as a raw material of biochar. The preparation of the oven-dried ECH sample before carbonization was similar with the previous research by (Rusnam *et al.*, 2022). The oven-dried ECH was carbonized at various heating temperatures, times and temperatures gradients. One parameter was varied while the other two parameters were kept constant.

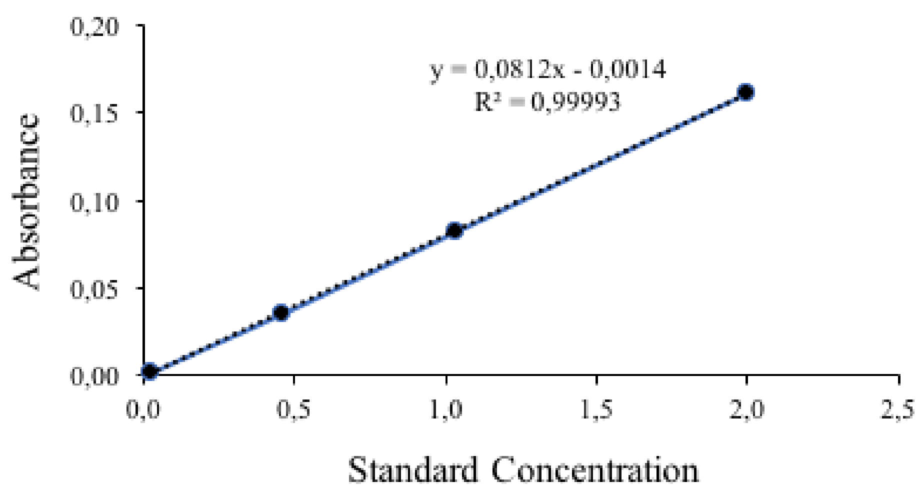

Figure 1. The standard curve of the Fe (ion) by ASS measurement

Table 1. The effect of carbonization parameter

Carbonization Parameter	Temperature (°C)	Time (h)	Rate (°C/min)
Carbonization Temperature	200 250 300 350 400 450 500 550 600	2	15
Carbonization Time	Maximum Carbonization Temperature	1 1.5 2 2.5 3	15
Carbonization rate	Maximum Carbonization Temperature	Maximum Carbonization Time	5 10 15 20 25

The temperature was varied in a range of 200 – 600 °C while the times and gradients were 1-3 h and 5 – 25 °C/min, respectively. The matrix for biochar preparation was designed and presented in Table 1. The sample was carbonized using muffle furnace (Nabertherm B180). During the carbonization, the sample was placed in ceramic crucible and covered with aluminum foil. The biochar was collected and sieved into particles < 50 µm after the carbonization ended and the furnace temperature was cooled down to room temperature.

2.3. Yield (%) and Ash Content (%)

The yield and ash content were determined for all condition of the ECH biochar (ECH-BC). The modified method by Aller *et al*. (2017) was occupied in this study to identify the ash content of the biochar. Furthermore, equation 1 and 2 were used to calculated the yield and ash content, respectively.

$$Y\ (\%) = \frac{W}{W_o} \times 100\% \tag{1}$$

$$\%\ Ash = \left(\frac{M_{ash}}{M_{OD-BC}}\right) \times 100\% \tag{2}$$

where W_o is the initial weight of the ECH before carbonization, and W is the final weight of ECH in a form of the biochar after carbonization. Meanwhile, M_{ash} is the mass in gram of the sample after heating, and M_{OD-BC} is the mass in gram of oven drying biochar before the heating.

2.4. Characterization of Biochar

IRTracer-100 Fourier Transform Infrared Spectrophotometer (FT-IR) (Shimadzu, Japan) was used to obtain IR spectra with a type Spectrum 100 series in the range of 4,000 - 400 cm-1. The data obtain was used to determine the characteristic of functional group on the surface of the ECH biochar at different temperature.

2.5. Biosorption Experiments

Biosorption experiments were carried out through batch studies by shaking 250 ml Erlenmeyer flask containing 100 mL of Fe (II) solution at concentration of 20 mg/L. The batch biosorption study was conducted for 2 h by setting up the orbital shaker machine (SK-0330 PRO Nesco Official) at a revolving speed of 150 rpm at ambient temperature. The mixture was filtered using filter paper (Whatman 42) and the concentration of Fe (II) in the solution after the filtration was determined by Atomic Absorption Spectrometry (AAS) (Shimadzu AA6800, Japan). Biosorption experiment of each type biochar was conducted triplicate and the average was used to determine the removal efficiency (RE) and adsorption capacity (q_t) of the biochar on Fe (II) using equations (3) and (4), respectively (Bhattacharyya & Gupta, 2008; Meroufel *et al.*, 2013) .

$$RE\ (\%) = \frac{C_o - C_t}{C_o} \times 100\% \quad (3)$$

$$q_t (\text{mg/g}) = \frac{(C_o - C_t)\,V}{m} \quad (4)$$

where, C_o is the initial concentration of Cd^{2+} (mg/L), C_t is concentration of Cd^{2+}, V is the volume of the solution (mL), and m is the mass of the biochar used (g) (Promariya *et al.*, 2021).

2.6. Data Analysis

A one-way analysis of variance (ANOVA) was conducted to determine the significance between the biosorption experiments under various ECH biochar. The program of statistical analysis system (SPSS Statistic 22.0) was used with the confidence level of the test was set at the 99% level with probability ($p < 0.01$). The normality test was done before performing the ANOVA test. Furthermore, the graphs were plotted from the average values of the triplicate biosorption experiments.

3. RESULTS AND DISCUSSION

The effect of the carbonization parameters of the chosen biomass and the targeted heavy metal ion were evaluated based on the performance of the biochar on reducing the heavy metal ion concentration in the water, and the percentage of the produced biochar at the specific carbonization process.

3.1. The Effect of Carbonization Temperature

- Yield and Ash Content

Table 2 showed the results of the percentage of yield and ash content of different parameters measured. It can be seen from the results that carbonization temperature plays a major role in the evaluation of ECH biochar preparation. As presented in Table 1, the percentage of yield was decreased with the increasing of carbonization temperature. As the lowest temperature applied in the experiment was 200 ºC, the highest yield was achived with 72.3 %. On the contrary, at the highest tempearture of 600 ºC, the lowest yield was obtained with 24.84%. Noteworthy, the significance decreased was noticed when the temperature increased from 200 ºC to 250 ºC and from 250 ºC to 300 ºC. At the mentioned increasing temperatures, the decreasing of yield were 11% and 18%, respectively, while at the other increasing temperatures in this experiment, resulted only the highest 5% of decreasing.

Meanwhile, the ash content of the biochar produced decreased when the applied temperature increased. The Table 2 showed the average value of ash content from triplicate measurements according to the implied measurement method. In contrast with the percentage of yield, the highest ash content found at temperature of 600 ºC with 5.5 ± 0.39 %, and the lowest one was at temperature 200 ºC with 5.8 ± 0.08%. The results obtained regarding to the percentage of yield and the ash content were aligned with the previous studies of various biomass types as reported by Yining *et al.* (2014) and Gao *et al.* (2015). The decrease in biochar yield at higher temperature is likely attributed to the increasing organic

Table 2. Yield and ash content of the ECH biochar at various carbonization temperature and carbonization time of 2h

Temperature of ECH Biochar (°C)	Yield (%)	Ash content (%)
200	72.3	5.5 ± 0.39
250	61.3	5.8 ± 0.08
300	43.6	9.7 ± 0.32
350	37.1	11.2 ± 0.22
400	35.4	12.9 ± 0.03
450	30.9	13.9 ± 0.11
500	27.3	14.8 ± 0.14
550	28.3	15.2 ± 0.25
600	24.8	17.5 ± 0.49

matter decomposition within the biomass. Yining *et al.* (2014) stated that the decreased in biochar yield at the higher temperature was probably because organic matter contained in the biomass decomposed more at the higher temperature. Furthermore, the significant decreasing of yield, when the temperature of 200°C and 250°C were decreased, was explained by Antal & Grønli (2003). The lost weight of the biochar when the temperature below 250 °C was mainly due to moisture and hydration water loss, while above 250°C, the biomass underwent decomposition and transform into vapor, comprising intricate organic compounds mixed with gases which consists of water vapor, carbon dioxide (CO_2), carbon monoxide (CO), hydrogen (H_2), methane (CH_4), and heavier hydrocarbons. Meanwhile, it is important to note that the ash content is typically dependent on the precursor, ECH.

- Biosorption Experiments

To explore the effect of the carbonization temperature on the properties of ECH biochar as BS for Fe ion, the triplicate batch biosorption studies were conducted and the average results were presented in Figure 2. The figure showed the graph of biosorption capacity (q_t) (mg/g) and removal efficiency (*RE*) (%) of the biochar at various temperatures in a range of 200 – 600 °C. Figure 2 clearly illustrated that the trend of RE and q_t generally increased with the increasing of temperature. However, it was noticed that the RE and q_t started dropped when the temperature was risen from 250 to 300 °C and 550 to 600 °C. At the lowest temperature of 200 °C, ECH biochar reached 27.8 ± 6.8 % of *RE* and 0.56 ± 0.13 mg/g of q_t. The number of RE and q_t were kept increasing to the higher temperature of 250°C, before further increased temperature to 300 °C resulted in significant declined of RE and q_t, from 31.1 ± 4.1 % to 8 ± 4 % and from 0.63 ± 0.08 to 0.11 ± 0.07, respectively. The finding was related to the decomposition of the biomass at the adjusted temperature which influence the properties of the pores of the produced biochar as discussed in the previous section of yield. Furthermore, previous finding Sun *et al.* (2020) showed that temperature above 300°C was the suggested temperature for carbonizing the biomass. Regarding to the findings, to determine the significance of the influence of carbonization temperature on Fe ion removal, therefore the results from 200°C and 250°C were not included in ANOVA analysis. The graph of the results without the two conditions was presented in Figure 3.

The highest RE and q_t were achieved at the biochar with the temperature of 550°C with 99.8 ± 0.1 % and 2.01 ± 0.02 mg/g, respectively. Theoritically, the increasing temperature will result in better pore formation due to the decomposition of cellulose and lignin which eventually give the higher *RE* and q_t. However, from the experimental results, when the temperature was further increased to 600 °C, the RE declined to 94.7 ± 4.1 % and the q_t dropped off to 1.92 ± 0.10 mg/g. It was explained in the study of Sun *et al.* (2020) that it was mainly because high temperature is beneficial for pore formation, however, higher temperature may result in the previous formed pores collapsed. In addition, the results were also integrated with the ash content mentioned in the previous section. The ash content is directly linked to the pore structure of the biochar. The higher ash content will resulted in less efficiency of adsorption,

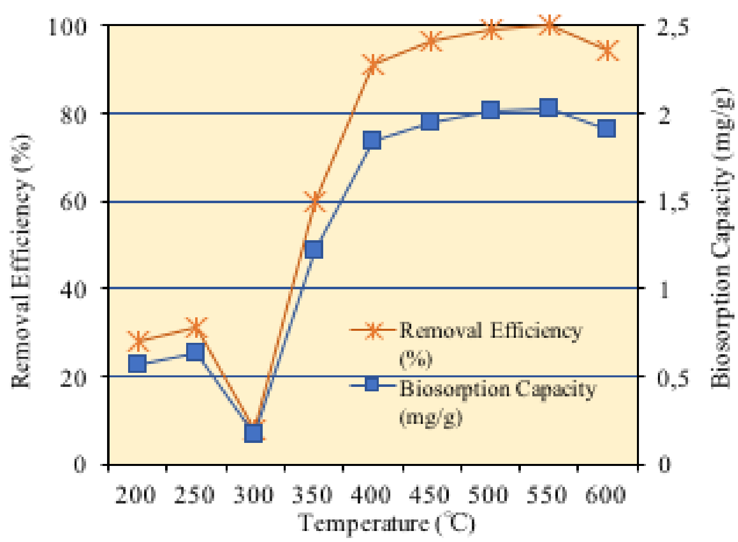

Figure 2. The data results of RE and q_t at various carbonization temperatures (200°C – 600°C) and at constant time of 2 h with the rate of 15°C/min.

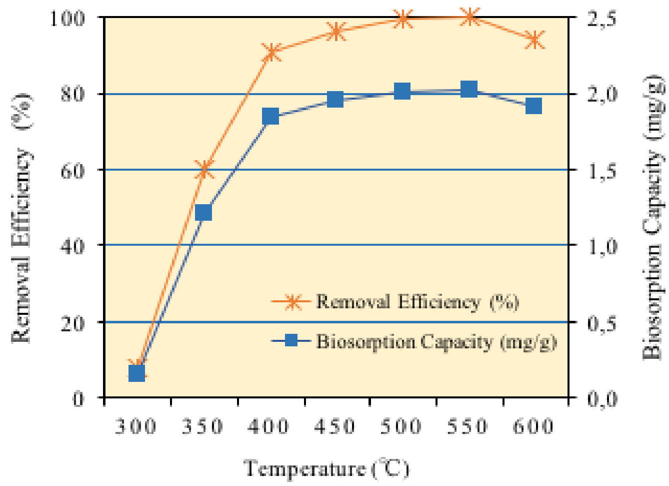

Figure 3. The data results of RE and q_t at various carbonization temperatures (300°C – 600°C) and at constant time of 2 h with rate of 15°C/min.

which from the results in Table 2, the ash content at temperature of 600 °C is higher than 550 °C which may the cause of the decreasing. Owing to the experimental results, therefore, it can be suggested that 550 °C gave the best results in the properties of ECH biochar as BS for Fe ion. The suggestion was supported by the outcome of ANOVA analysis with $p < 0.01$ where the result showed that the temperature had a significant effect on the biochar properties.

3.2. The Effect of Carbonization Time

- Yield and Ash content

The effect of carbonization time on the percentage of yield and ash content of the biochar from ECH were presented in Table 2. The comparison of yield at the lowest temperature of 1 h with the highest temperature of 3 h showed that the longer temperature resulted in less yield. However, it was shown in the Table that the percentage of yield in general was fluctuate under a constant temperature of 550°C with the longer time of carbonization time. This trend was similar with the study by Sun *et al.* (2017) that investigated the effect of residence time of the different biomass. Owing to the obtained results from the experiment and supported by the previous finding, it is suggested that carbonization time had a little effect on the biochar yield. This is mainly due to during the longer time, no further decomposition is conducted mainly only biochar surface and internal structure change. Meanwhile, the ash content was seen in an increasing trend with the longer time carbonization of the biomass. It was also discussed in the previous finding of Sun *et al.* (2017), that as the residence time increased, irregular carbon originally retained in the charred feedstock would be selectively consumed, hence developing in microcrystalline and enlarging the specific surface area of biochar.

Table 2. Yield and ash content of the ECH biochar at various carbonization time and constant temperature of 550 °C.

Time of ECH Biochar (Hour)	Yield (%)	Ash Content (%)
1.0	28.8	10.8 ± 1.24
1.5	29.9	11.1 ± 0.15
2.0	27.3	11.2 ± 0.28
2.5	26.1	11.5 ± 0.16
3.0	27.4	11.6 ± 0.17

- Biosorption Experiments

Regarding the effect of the different carbonization time on the performance of the ECH biochar for Fe ion removal, various RE and q_t were obtained and presented in Figure 4. The temperature was set at 550°C while the temperature gradient of 15°C/min. It can be seen from the Figure that longer time resulted in varied *RE* and q_t. The extension of carbonization did not always give the similar trend. The decreasing trends were noticed when the time was extended from 1.5 h to 2h and 2.5 h to 3 h. The extension from 1.5 h to 2 h declined the *RE* and q_t from 99.5 ± 0.00 % to 98.9 ±0.06 % and 1.76 ± 0.02, respectively. Meanwhile the longer time of carbonization from 2.5 h to 3 h decreased the results from 99.4 ± 0.16 % to 99.0 ± 0.25 % for Re and from 1.76 ± 0.01 to 1.75 ± 0.01 for qt. Owing to mentioned experimental results, 1.5 h is suggested as the most suitable carbonization time of ECH biochar for Fe ion. Even though the time of 2.5 h also showed the possibility of the most suitable one, however by comparing the *RE* and q_t and from the economic point of view, the carbonization time of 1.5 h resulted in slightly higher of *RE* and q_t. The outcomes of *RE* and q_t were in agreement with the yield where the carbonization time had a little effect on the properties of ECH bochar as biosrobent for Fe ion. The suggestion was supported by the outcome of ANOVA analysis with p 0.019 where the result showed that cabonization time had no significant effect on the biochar properties.

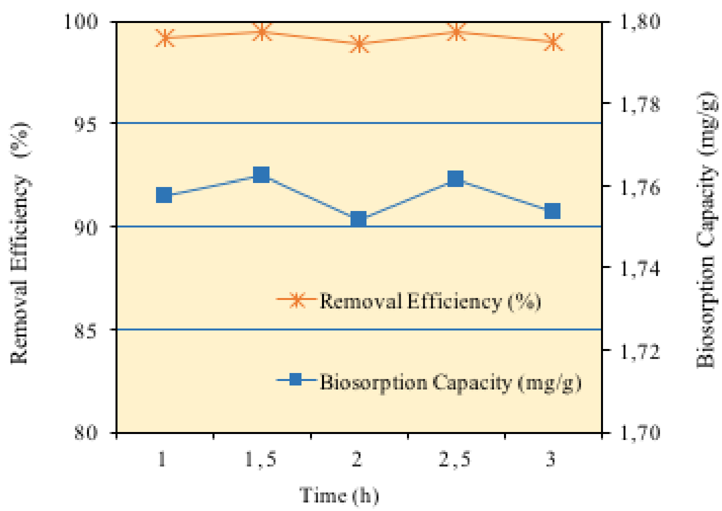

Figure 4. Effect of carbonization time on the *RE* and q_t at constant temperature (550 °C) and temperature gradient (15 °C/min).

Table 3. Yield and ash content of the ECH biochar at various carbonization rate

Temperature gradient of ECH Biochar (°C/min)	Yield (%)	Kadar Abu (%)
5	28.9	17.6 ± 0.37
10	29.4	17.2 ± 1.04
15	29.9	11.1 ± 0.15
20	27.0	14.8 ± 0.42
25	26.6	19.4 ± 0.96

3.3. The Effect of Temperature Gradient

- Yield and Ash Content

Unlike the other two parameters, the effect of carbonization gradient of time on the properties of the biochar is rarely studied. In this experimental study, the gradient of time was varied at the constant temperature of 550°C and time of 1.5 h. Table 3 presented the yield and ash content in percentage of the varied biochar.

The outcomes indicated the similarity effect of the carbonization gradient of time with the one from the carbonization time. Regarding to the results, it can be suggested that the gradient of time had a little effect on the biochar yield and the ash content of the biochar.

- Biosorption Experiments

In this study, the effect of carbonization rate on the properties of ECH biochar was studied at the various rate with the constant temperature of 550 °C and time of 1.5 h. The batch experiment of ECH biosorption on Fe ion at the different gradient of time gave the various *RE* and *qt* as seen in Figure 5. It showed all carbonization rates resulted in the high *RE* and q_t. Furthermore, the linear relation was seen between the gradient of time and the obtained *RE* and q_t. The higher gradient of time resulted in the higher RE and q_t. In this experimental study, the highest *RE* and *qt* were obtained at the rate of 25 °C/min. The gradient was belong to slow carbonization (10 °C/s) (Zhou *et al.*, 2019). Regarding to the ANOVA analysis, where the result showed that gradient of time had no significant effect on the biochar properties as the p value was 0.839.

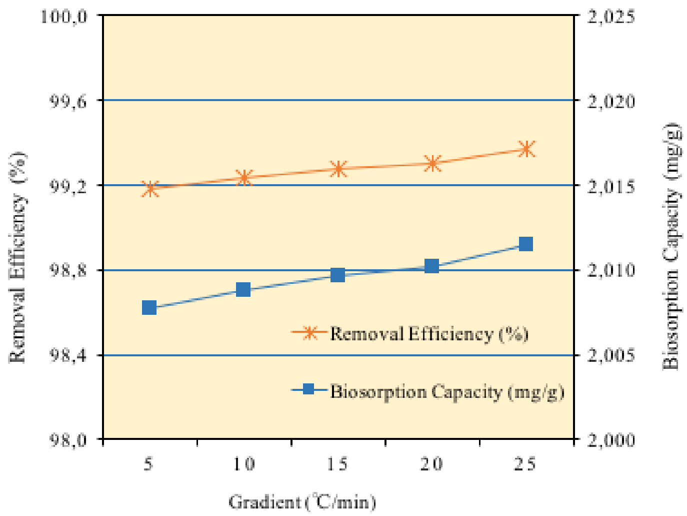

Figure 5. The *RE* and q_t of various temperature gradient (5 – 25 °C/min) at constant temperature 550 °C and time of 1.5 h.

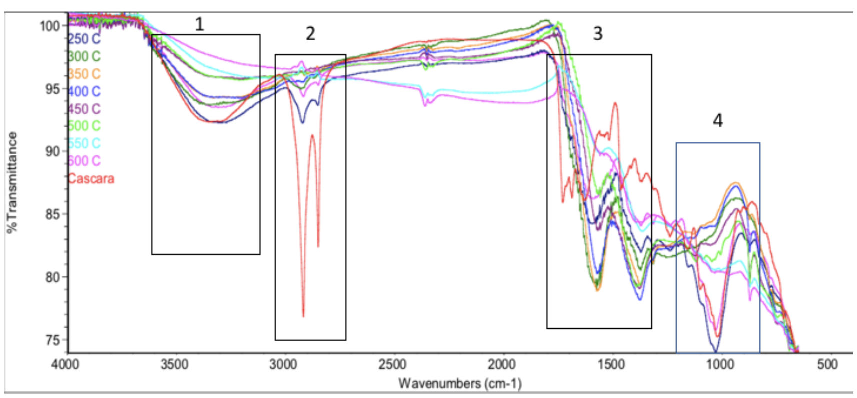

Figure 6. The FT-IR spectra of ECH biochar at various carbonization temperature.

3.4. Characterization of the ECH biochar

FT-IR spectra of the ECH biochar at different temperature were measured to analyze the functional groups. The spectra were overlaid and presented in Figure 6. The figure showed the FTIR spectra of ECH biochar from the various temperature in a range of 200˚C – 600˚C in the region of 4000 – 400 cm^{-1}. Looking from an overall view, the vibrational intensity of the peaks decreased with an increasing of the carbonization temperature. The spectrum of raw ECH displayed four notable peaks, in the region between 3600 and 3100 cm^{-1}, 2970-2861 cm^{-1}, 1738 and 1630 cm^{-1}, and 1034–1036 cm^{-1}. The broad peak in the region of 3600 and 3100 cm^{-1} was attributed to O-H stretching in absorbed water, lignin, and cellulose, while the other three were attributed to C-H vibrations in methyl and methylene groups, C—C bond of aldehyde, C-O stretching in carboxyl group, C-O-C, dialkyl ether, C-H of aromatics, and C=C and C-C-O, respectively (Üner & Bayrak, 2018).

It can be seen from the spectra displayed in the Figure 6, there were shifted peaks by the increasing of carbonization temperature. The peak (2) was disappeared as the carbonization temperature rose from 250 to 300˚C. The present of the peak with lower intensity of the ECH biochar of 200˚C and 250˚C might be one of the cause the RE and q_t at both temperatures were higher than the one at 300˚C. The similar trend was also seen for the peak (4). It was also stated in the report of Çelebi, Gök and Gök (2020) that the present functional groups bring surrounding ions together and supply protons to the liquid medium. Eventually, the surface complexes are formed between metal ions and functional groups as the electron-pair acceptor metal ions are in question.

4. CONCLUSIONS

The research concluded that the temperature had a significant effect on the properties of the ECH biochar as BS for Fe (II) while carbonization time and rate has a little effect. The carbonization temperature of 550°C has the highest performance of the biochar while the time of 1.5 h of time and 25 °C/min are the highest ones for each parameter. Furthermore, the effect of carbonization temperature is also noticed on the functional groups on the ECH biochar.

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