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Characterization of Activated Carbon from Rice Husk by HCl Activation and Its Application for Lead (Pb) Removal in Car Battery Wastewater

F Hanum*, O Bani, and L I Wirani

Chemical Engineering Department, Faculty of Engineering, Universitas Sumatera Utara, Medan 20155

*ida_hanum1978@yahoo.com

Abstract. Activated carbon is highly porous carbon which has been treated to increase its adsorption performance. Rice husk, due to its high cellulose and lignin content, can be used as source of carbons to produce activated carbon. This research aims to evaluate the effects of carbonization time and temperature on activated carbon production from rice husk and its application for lead (Pb) adsorption in car battery wastewater. In this research, dried rice husk was carbonized at 400–600 °C under constant nitrogen flow for 90 minutes to 150 minutes, followed by chemical treatment using HCl. Dried activated carbons was sieved to 100 meshes prior to application. Result indicated that maximum carbon yield of 49.33% was obtained at carbonization temperature of 500 °C and carbonization time of 150 minutes. The activated carbon contained 4.86% moisture, 30.04% ash, and 15.76% volatile matter. The adsorption capacity was found to be 0.56731mg/g with percentage removal 54.85%.

1. Introduction

Indonesia is one of many countries with large rice consumption in the world. Most of Indonesia's population consume rice as staple food [1]. In 2015, the unhusked rice production in Indonesia reached 4.04 million tons (dry base), increased by 413.790 tons compared to the production in 2014 [2]. As consequence, the amount of rice husk generated will increase as well. Rice husk contains 32% cellulose, 21% hemicellulose, 22% lignin and 15% ash [3]. Due to its composition, it suits to be used as carbon source to produce activated carbon with specific pore structure and surface area [4, 5].

Activated carbon is referred to carbonaceous materials, with high physico chemical stability, high porosity, high sorption capacity and immense surface area [6]. Activated carbon consist of 87–97% carbon and other trace elements at various concentrations, depends on the method and process used [7]. Activated carbon has obviously been the greatest and widely used material for treatment of wastewater pollution which can adsorp some kinds of heavy metals such as copper, lead, cadmium, and chromium [8]. Heavy metals are not biodegradable and can lead to accumulation in living organisms, causing various diseases and disorders [9]. The preparation of activated carbon with different pore sizes can be achieved by physical or chemical activation process [10].

Some researches about activated carbon from rice husk had been performed before. Liyana (2013) used NaOH to activate rice husk based adsorbent to adsorb metal ions from aqueous solution. Results showed that rice husks can be used as adsorbent to adsorb some heavy metal ions [5]. Kumar and

Acharya (2011) studied about Pb adsorption using rice husk adsorbent activated with sodium carbonate. The results showed that rice husk is a good adsorbent to adsorb lead (Pb) [11].

There are many researches about activated carbon from rice husk, but none had focused on the optimum carbonization temperature and time using hydrochloric acid (HCl) as activator for lead (Pb) adsorption. Hydrochloric acid is hygroscopic chemical activator that promote dehydration, reducing moisture content from activated carbon produced [12]. This research aims to determine the optimum carbonization temperature and time to produce activated carbon from rice husk using HCl activator and its application for lead (Pb) removal in car battery Wastewater. This study would contribute knowledge for those who work in the car battery wastewater treatment to use economical and natural material for making activated carbon under advanced process.

2. Materials and Methods

2.1. Materials and Instrumentations

The apparatus used in this study consisted of furnace equipped with nitrogen stream, oven, porcelain cup, desiccator, aluminum foil, whatman paper no. 40, digital balance, beaker glass, measuring cylinder, funnel glass, 100 mesh sieve, muffle furnace, AAS, and SEM.

The materials used in this study were rice husk, hydrochloric acid, nitrogen, distilled water, car battery wastewater.

Rice husks were collected from rice mill at Kuta Buluh Simole Village Kec Kuta Buluh Simole Kab. Karo Sumatera Utara. Hydrochloric acid was purchased from Merck. Nitrogen was purchased from PT. Utama Gas. Car battery wastewater was obtained from industry home Samsin battery at Jl. Balai Desa Kec. Medan Polonia.

2.2. Preparation of Activated Carbon

Rice husks were repeatedly washed using distilled water to remove existing impurities on the surface and dried in oven at 110 °C for 3 hours. After that, 25 g dried rice husk was carbonized in the furnace at 400, 450, 500, 550, and 600 °C for 90, 120, and 150 minutes. Then, it was impregnated with hydrochloric acid 5% (v/v) at carbon to acid ratio of 1:10 (w/v) for 24 hours. Afterwards, it was filtered and oven dried at 110°C for 3 hours, followed by sieving to 100 meshes.

2.3. Characterization of Activated Carbon

Activated carbon was characterized to determine the basic properties of activated carbon from rice husk. The characterization includes the analysis of moisture, ash, volatile matter, and fixed carbon content. Standard specification for activated carbon in accordance with Indonesian Standard (SNI No. 06-3730-1995) is presented in the Table 1 [13].

Table 1. Standard Specification for Activated Carbon

Analysis	Quality Requirements	
	Particle	Powder
Volatile matter 950 °C, %	Max.15	Max. 25
Moisture content, %	Max. 4,5	Max. 15
Ash content, %	Max. 2,5	Max. 10
Parts that are not carbonized	0	0
Iodine Number, mg/g	Min. 750	Min. 750
Pure activated carbon, %	Min. 80	Min. 65
Benzene adsorption capacity, %	Min. 25	-
Methylene blue Number, mg/g	Min. 60	Min. 120
Bulk specific gravity, g/ml	0,45 – 0,55	0,3 – 0,35
Escaped mesh 325, %	-	Min. 90
Distance, %	90	-
Violence, %	80	-

2.3.1. Moisture Content Analysis

As much as 1 g of activated carbon was placed in a porcelain cup. It was then heated in an oven at 105–110 °C for 1.5 hr. Then, sample was cooled in desiccator and the weight of dried sample was measured. Moisture content was calculated as follow [14]:

$$\mathrm{M} = \frac{\mathrm{B} - \mathrm{F}}{\mathrm{B} - \mathrm{G}} x\ 100$$

Where,
B = weight of porcelain + original sample
F = weight of porcelain + dried sample
G = weight of porcelain

2.3.2. Ash Content Analysis

As much as 1 g of activated carbon was placed in a porcelain cup. It was heated in a muffle furnace at 750 °C for 1.5 hr. Then sample was cooled in desiccator and the weight of the ash was measured [14].

$$\mathrm{A} = \frac{\mathrm{F} - \mathrm{G}}{\mathrm{B} - \mathrm{G}} x\ 100$$

Where,
G = mass of empty porcelain
B = mass of porcelain + sample
F = mass of porcelain + ash sample

2.3.3. Volatile Matter Content Analysis

As much as 1 g of activated carbon was placed in a porcelain cup. It was heated at 925 °C for 7 minutes in a muffle furnace. Then porcelain was cooled in desiccator and the weight of the sample was measured [14].

$$\mathrm{Vm} = \frac{[100(B - F) - M(B - G)]}{(\mathrm{B} - \mathrm{G})(100 - \mathrm{M})} x\ 100$$

Where,
B =mass of porcelain, lid and sample before heating

F = mass of porcelain, lid and contents after heating
G = mass of empty porcelain & lid
M = % of moistures determine above

2.3.4. Fixed Carbon Content
Fixed carbon (FC) content was calculated as follow [14]:
FC = 100 - (%M + %A + %Vm)

2.4. Adsorption of Lead (Pb)
The adsorption is conducted by adding 1 gram (g) activated carbon to 100 ml battery car wastewater and stirred at 60 rpm for 30 minutes then filtered. Adsorbed lead was analyzed using Atomic Adsorption Spectrometry (AAS).
Adsorption capacity was calculated using the equations [15]:

$$Qe = \frac{(Ci - Ce)}{M} \times V$$

$$\% R = \frac{100(Ci - Ce)}{Co}$$

Where,
Qe = adsorption capacity (mg/g)
Co = initial metal concentration (mg/l)
Ce = final metal concentration (mg/l)
W = adsorbent mass (g)
V = volume of metal solution (l)
R = the percentage of removal Pb ions

3. Results and Discussion

3.1. Characterization of Activated Carbon from Rice Husk
Characteristic of activated carbon such as moisture content, ash content, volatile matter and fixed carbon was determined on this research. Table 2 shows results of activated carbon characterization.

Table 2. Results of Activated Carbon Characterization

No	Carb. Temp (ºC)	Carb. Time (minutes)	Moisture (%)	Ash (%)	Volatil Matter (%)	Fixed Carbon (%)
1	400	90	6.20	28.30	22.68	42.82
2		120	6.17	29.12	19.13	45.59
3		150	6.03	29.77	17.20	47.00
4	450	90	5.87	29.93	21.62	42.59
5		120	5.71	30.32	19.01	44.96
6		150	5.68	29.80	16.44	48.09
7	500	90	5.31	31.40	21.26	42.02
8		120	5.14	31.51	18.78	44.57
9		150	4.86	30.04	15.76	49.33
10	550	90	4.53	32.22	20.09	43.16
11		120	4.16	33.26	18.37	44.21
12		150	3.92	31.76	15.51	48.81
13	600	90	3.81	34.17	19.66	42.37
14		120	3.64	35.77	17.55	43.04
15		150	3.48	36.80	15.30	44.42

3.2. Effect of Carbonization Temperature and Carbonization Time on Moisture Content

Moisture content is the amount of water in samples. Determination of moisture content aims to determine the hygroscopic properties of carbon [1].

The effect of carbonization temperature and carbonization time on moisture content of activated carbon from rice husk is shown in Fig. 1.

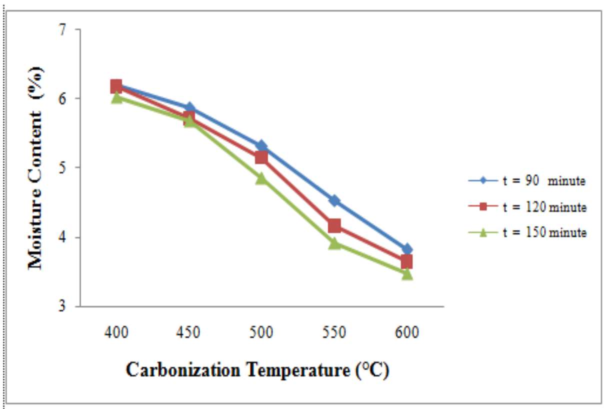

Figure 1. Effect of Carbonization Temperature and Carbonization Time on Moisture Content

From Fig. 1, moisture content tends to decrease as carbonization time increases. As carbonization proceeds, more pores unclog and more moisture is liberated from the carbon [1]. Higher carbonization temperature and time also led to lower moisture content.

All sample moisture content met the standards for activated carbon based on Indonesian Standard (SNI No. 06-3730-1995) that maximum at 15%.

3.3. Effect of Carbonization Temperature and Carbonization Time on Ash Content

Ash content is used to determine the quality of activated carbon. Ash content refers to residual minerals in activated carbon after carbonization and activation process [16].

The presence of ash leads to blockage of the pores which reduces the surface area of activated carbon [1]. The effect of carbonization temperature and carbonization time on ash content of activated carbon from rice husk is shown in Fig. 2.

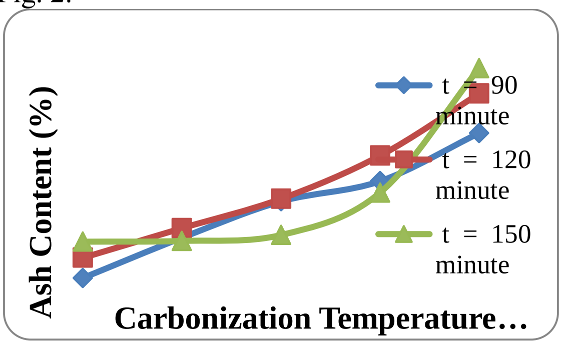

Figure 2. Effect of Carbonization Temperature and Carbonization Time on Ash Content

As seen in Fig. 2, ash content tends to increase with carbonization temperature. This result agrees with that reported by Siahaan et al. (2013) in which the ash content increased along with carbonization temperature [1].

Increasing the temperature and time of carbonization, the resulting ash content increases. The ash content of all activated carbon produced did not meet to Indonesian Standard (SNI No. 06-3730-1995) that maximum at 10%.

3.4. Effect of Carbonization Temperature and Carbonization Time on Volatile Matter Content

The amount of volatile matter corresponds to compounds that have not evaporated during carbonization, but evaporates at 950 °C [1].

The effect of carbonization temperature and carbonization time on volatile matter content of activated carbon from rice husk is shown in Fig. 3.

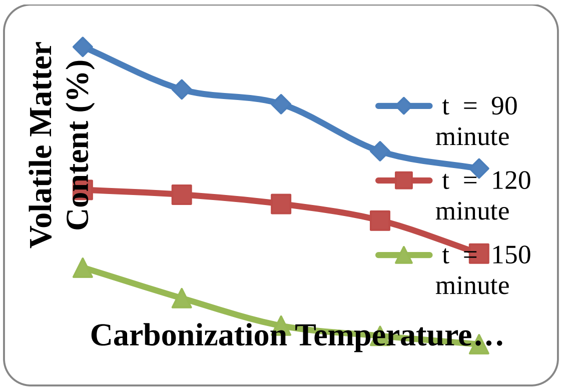

Figure 3. Effect of Carbonization Temperature and Carbonization Time on Volatile Content

As in Fig. 3, it can be observed that volatile matter content tends to decrease with the increase of carbonization temperature from 90–150 minutes. The result is consistent with that obtained by Siahaan (2013), which longer carbonization time decrease then levels of volatile matter [1].

All sample volatile matter content meet the standards for activated carbon based on Indonesian Standard (SNI No. 06-3730-1995) that maximum at 25%.

3.5. Effect of Temperature and Time Carbonization on fixed carbon

Figure 4 shows a graph of the effect of temperature and time carbonization on fixed carbon of activated carbon from rice husk. Carbon content is the amount of pure carbon contained in the carbon [1].

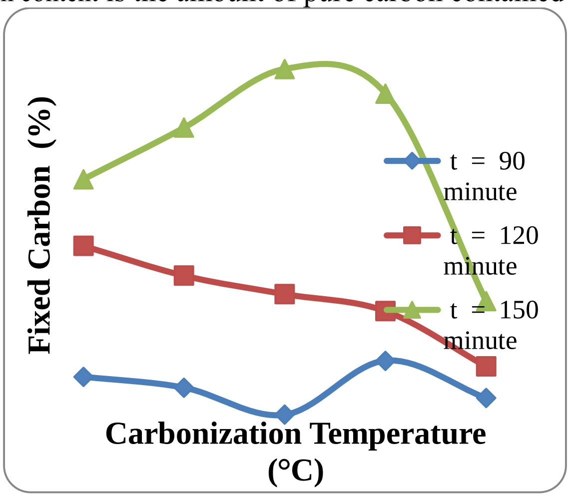

Figure 4. Effect of Temperature and Time of Carbonization on fixed carbon

It can be seen from Figure 4 above that the fixed carbon content of activated carbon from rice husk fluctuates along with the increasing of carbonization temperature. This condition occured because the carbonization process at high temperature (500 ^{o}C – 600 ^{o}C) tends to damage the pore walls of carbon thus reducing the yield of carbon [1].

The highest carbon content obtained at a temperature of 500 ° C for 150 minutes was 49.33% and the lowest volatile matter content obtained at 500 ^{o}C for 90 minutes. Fixed carbon obtained does not meet the quality standards of activated carbon based SNI No. 06-3730-1995 is at least 65%.

3.6. Scanning Electron Microscope (SEM) Analysis

The surface morphology of rice husk, carbon of rice husk before activated and activated carbon using physics-chemical processes were identified using SEM-EDS at 600 x magnification objects. The results can be seen in the following figure.

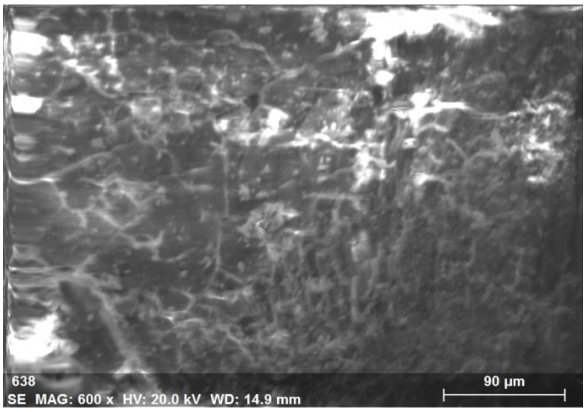

Figure 5.SEM of Rice Husk

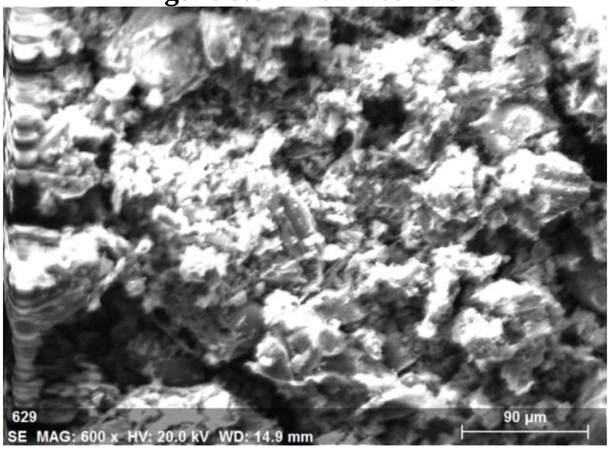

Figure 6.SEM of Rice Husk after Carbonization

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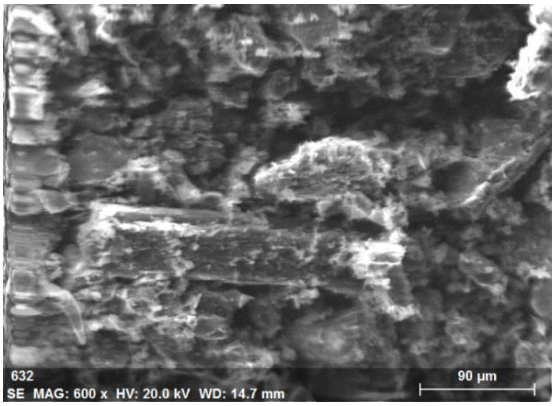

Figure 7. SEM of Activated Carbon

Based on the figure 5, 6 and 7 above, it can be seen the difference of the surface morphology of rice husks, carbons before activated and activated carbon physico-chemical processes. The pore surface structure of the surface morphology of rice husk (figure 5) can't be seen.

The surface morphology of carbon before activated (figure 6) can be seen the distribution of pores but they seems to have a lot of impurities so that the pores are hard to see. While activated carbon using physics-chemical processes (Figure 7) shows their pores and impurities inherent in the surface looks fewer than carbon before activated.

This is because the activation using HCl can dissolve impurities so the pores more established and adsorption processes become maximum [17]. The SEM results shows that the surface activated carbon using physics-chemical processes contains well-developed pores where can be used as adsorbent to adsorb lead ions in car battery wastewater.

3.7. Energy Dispersive Spectroscopy (EDS) Analysis

The EDS spectra showing elemental composition were obtained by scanning through the surfaces of the samples characterized [18]. EDS can be used to analyze quantitatively the percentage of each element as shown in the following figures and tables.

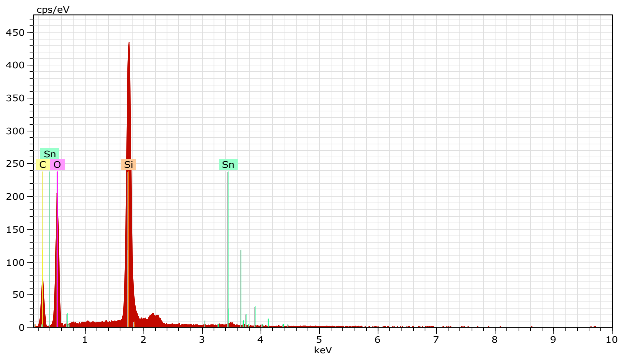

Figure 8. EDS of Rice Husk

Table 3. EDS of Rice Husk

Spectrum: SEKAM PADI

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]
O	8	K-series	34.64	46.18	45.84
C	6	K-series	23.87	31.83	42.08
Si	14	K-series	15.86	21.15	11.96
Sn	50	L-series	0.63	0.84	0.11
		Total:	75.00	100.00	100.00

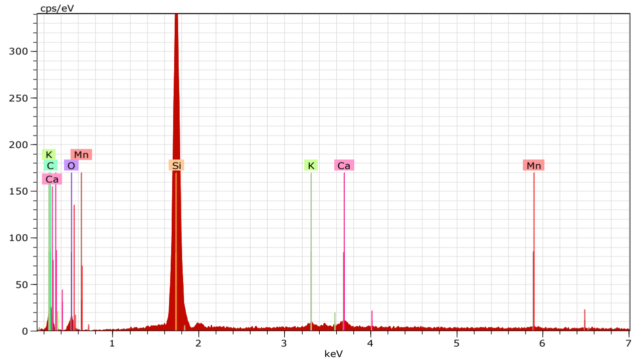

Figure 9. EDS of Rice Husk After Carbonization

Table 4. EDS of Rice Husk After Carbonization

Spectrum: Karbon

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]
Si	14	K-series	21.46	43.34	26.72
C	6	K-series	19.42	39.23	56.57
O	8	K-series	7.03	14.20	15.37
Ca	20	K-series	0.76	1.55	0.67
K	19	K-series	0.54	1.10	0.49
Mn	25	K-series	0.29	0.59	0.19
		Total:	49.51	100.00	100.00

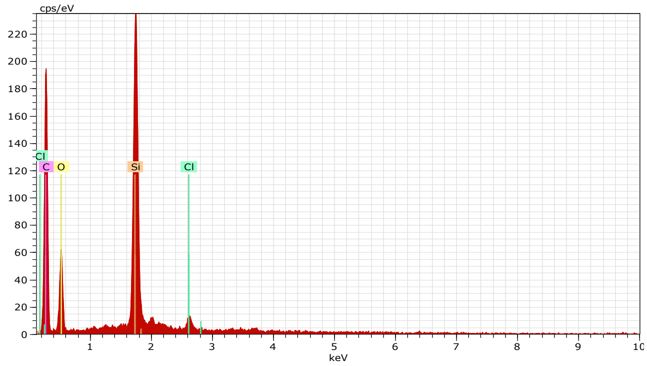

Figure 10. EDS of Activated Carbon

Table 5. EDS of Activated Carbon

Spectrum: HCL KARBON AKTIf FK

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]
C	6	K-series	48.90	63.39	73.02
O	8	K-series	18.76	24.32	21.03
Si	14	K-series	8.70	11.28	5.56
Cl	17	K-series	0.78	1.01	0.40
		Total:	77.14	100.00	100.00

Based on the EDS results, it can be observed that rice husk (table 3) contains 45.84% O, 42.08% C, 11.96% Si and 0.11% Sn. Rice husk after carbonization (table 4) contains 15.37% O, 56.57% C, 26.72% Si, 0.67% Ca, 0.49% K and 0.19% Mn. Activated carbon after physical-chemical processes (table 5) contains 73.02% C, 21.03% O, 5.56% Si and 0.40% Cl.

These results indicate that the carbon elements contained in rice husk, rice husk after carbonization and activated carbon physic-chemical process have developed so that activated carbon at physic-chemical process qualify the standards of activated carbon by SNI No. 06-3730-1995 with minimum value 65% of carbon.

3.8. Adsorption of Pb in Car Battery Industry Wastewater

Concentration of metallic lead (Pb) before and after adsorption is analyzed using Atomic Adsorption Spectrometry (AAS). The activated carbon used was carbonized at 500 °C for 150 minutes. The initial concentration of wastewater (before adsorption) is 10.3437 mg/l, while the final concentration (after adsorption) of wastewater is 4.6706 mg/l. Concentration before and after adsorption obtained were used to calculate the capacity of adsorption lead (Pb) ions of activated carbon from rice husk.

Adsorption capacity is the ability of adsorbent to adsorb some metals expressed as a number of adsorbat mg per 1 gram of adsorbent. Adsorption capacity obtained at 0.56731 mg/g with a percentage of 54.85%. Low absorption capacity of metal ions of lead (Pb) in the adsorbent can occur due to other metals such as chromium (Cr), copper (Cu), zinc (Zn), nickel (Ni) and cadmium (Cd) in the wastewater of industry battery car having competition in the heavy metal adsorption process.

4. Conclusion

Maximum condition of carbonization obtained at temperature of 500 °C and time of 150 minutes with moisture content of 4.86%, ash content of 30.04%, volatile substance content of 15.76% and fixed carbon content of 49.33%. At high of temperature, moisture content and the level of volatile substance produced will decrease. The increased temperature and carbonization time leads to high of ash content. The adsorption capacity obtained was 0.56731 mg/g with percentage removal of 54.85%.

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