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Characterization of Sodium Carbonate (Na_2CO_3) Treated Rice Husk Activated Carbon and Adsorption of Lead from Car Battery Wastewater

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Abstract. The use of rice husk as adsorbent would not only reduce its disposal problems, but would also produce value-added products, such as activated carbon derived from rice husk. This study aimed to determine the optimum carbonization temperature for activated carbon production from rice husk and its adsorption performance on Pb in car battery wastewater. In this study, activated carbon was produced by carbonizing rice husk 400–600 °C for 90–150 minutes followed by chemical activation using 5% Na_2CO_3 and sieving to 100 meshes. Lead adsorption was measured using atomic absorption spectroscopy (AAS). Results suggested that highest carbon yield of 47.75% was obtained for carbonization at 500 °C for 150 minutes. At that condition, produced activated carbon contained 3.35% moisture, 30.86% ash, 18.04% volatile matter. The adsorption capacity was found to be 0.6007 mg lead/g adsorbent with % adsorpsi 58.08%

1. Introduction

Activated carbon (AC) is a carbonaceous material that can bee prepared by the pyrolysis and having high specific porosity, high surface areas extremely versatile adsorbent of major industrial significance [1, 2]. Activated carbon which have been used for the removal of heavy metals and dyes from wastewater [3].

The most precursors used for the production of activated carbon are organics material that are rich in carbon [4]. In recent years, a lot of research has been reported on activated carbon from agricultural wastes such as rice husk [5-8], acorn shell [9], peanut shell [10], pine cone [11], coconut husk [12], coffee husk [13], coffee residue [14], tea [15], etc.

The annual world production is about 571 million tonnes resulting in approximately 140 million tonnes of rice husk available annually for utilization [16]. The use of rice husk as adsorbent would not only reduce its disposal problems, but would also produce value-added products, such as activated carbon derived from rice husk [8].

Table 1. Typical Composition of Rice Husk [17]

Composition	Percent
Cellulose	32.24
Hemicellulose	21.34
Lignin	21.44
Extractives	1.82
Water	8.11
Mineral ash	15.05
Chemical composition in mineral ash:	
SiO_2	96.34
K_2O	2.31
MgO	0.45
Fe_2O_3	0.2
Al_2O_3	0.41
CaO	0.41
K_2O	0.08

There are two method for the preparation of activated carbon one is physical activation and second is chemical activation. The most commonly used chemical activating agents are KOH, H_2SO_4, $ZnCl_2$, Na_2CO_3, K_2CO_3, NaOH, H_3PO_4, [10] etc. KOH, K_2CO_3 and Na_2CO_3 are usually use for activating residue shich in rich ash [7]. This study aimed to determine the optimum carbonization temperature for activated carbon production from rice husk and its adsorption performance on Pb in car battery wastewater.

2. Material and Methods

2.1. Material and Instrumentations
Rice husk (*Oryza sativa L.*) was obtained Kuta Buluh Simole village Kec. Kuta Buluh Simole Kab. Karo Sumatera Utara. Sodium Carbonate was purchased from Merck, Nitrogen was purchased from Utama Gas, and car battery wastewater was obtained from Samson battery industry home at Jl. Balai Desa Kec. Medan Polonia.

The apparatus used in this study consisted of furnace equipped with nitrogen stream, oven, muffle furnace, digital balance, desiccator, erlenmeyer, beaker glass, measuring cylinder, funnel glass, 100 mesh sieve, porcelain, alumunium foil, Whatman paper No. 40.

This work had as a main objective to obtain activated carbon from rice husk and to analyze their internal structure through Scanning Electronic Microscopy (SEM), AAS and EDS (Energy Dispersive Spectroscopy).

2.2. Preparation of Activated Carbon
Rice husks were repeatedly washed with distilled water to remove existing impurities on the surface and oven dried 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 min. Then, it was impregnated with sodium carbonate (Na_2CO_3) 5% (w/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 from Rice Husk
Standard specification for activated carbon in accordance with Indonesian Standard (SNI No. 06-3730-1995) is presented in the Table 2 [18].

Table 2. Standard Specification of 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	,45 – 0,55	),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 [19]:

$$\mathrm{M} = \frac{\mathrm{B-F}}{\mathrm{B-G}} x\ 100 \qquad (1)$$

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 [19].

$$\mathrm{A} = \frac{\mathrm{F-G}}{\mathrm{B-G}} x\ 100 \qquad (2)$$

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 mins in a muffle furnace. Then porcelain was cooled in desiccator and the weight of the sample was measured [19].

$$\mathrm{Vm} = \frac{[100(B-F)-M(B-G)]}{\mathrm{(B-G)(100-M)}} x\ 100 \qquad (3)$$

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 determined above

2.3.4. Fixed Carbon Content. Fixed carbon (FC) content was calculated as follow [19]:

FC = 100-(%M + %A + %Vm) (4)

2.4. Adsorption Of Lead From Car Battery Wastewater
The adsorption is conducted by adding 1 g activated carbon to 100 ml battery car wastewater and stirred at 60 rpm for 30 mins then filtered. Adsorbed lead was analyzed using Atomic Adsorption Spectrometry (AAS).

Adsorption capacity was calculated using the equations [14]:

$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad (5)$$

$$\%removal = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \quad (6)$$

Where:
Qe=adsorption capacity (mg/g)
Co=initial metal ion concentration (mg/L)
Ce=equilibrium metal ion concentration (mg/L)
M = weight of adsorbent (g)
V = volume of aqueous solution (L)

3. Results and Discussions

3.1. Characterization of Activated Carbon from Rice Husk
Characterization of activated carbon is summarized in Table 3.

Table 3. Result Characterization of Activated Carbon from Rice Husk.

No	Carbonization Temperature (°C)	Carbonization Time (minute)	Moisture (%)	Ash (%)	Volatile Matter (%)	Fixed Carbon (%)
1	400	90	5.64	28.80	23.11	42.45
2	450		4.91	29.52	22.80	42.77
3	500		4.01	30.31	21.28	44.40
4	550		3.28	31.00	19.65	46.07
5	600		3.00	32.78	18.85	45.37
6	400	120	5.51	29.10	21.53	43.86
7	450		4.68	29.69	20.56	45.07
8	500		3.74	30.53	19.09	46.64
9	550		3.17	31.22	18.63	46.98
10	600		2.73	32.91	18.68	45.68
11	400	150	5.16	29.41	19.87	45.56
12	450		4.45	29.99	20.21	45.35
13	500		3.35	30.86	18.04	47.75
14	550		3.10	32.55	18.35	46.00
15	600		2.47	33.05	18.03	46.45

3.1.1. Effect of Carbonization Temperature and Carbonization Time on Moisture Content. Moisture content aims to determine hygroscopic properties of carbon [20]. The effect of carbonization temperature and carbonization time on moisture content of activated carbon from rice husk is shown in Fig. 1.

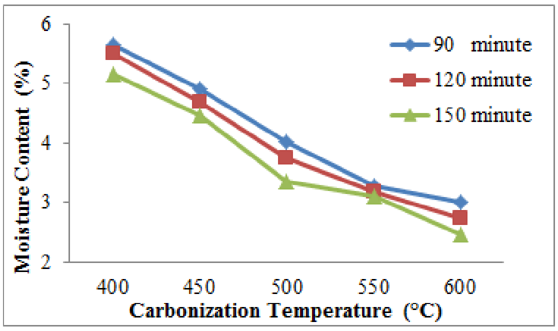

Figure 1. Effect of Carbonization Temperature and Carbonization Time on Moisture Content

From Fig. 1, moisture of activated carbon decreases with increasing carbonization time and temperature.

This result same as with that reported by Siahaan et al. (2013) in which the moisture content decrease along with carbonization temperature. Increasing the temperature and time of carbonization, the resulting moisture content decreaase. All sample moisture content suitable the standards for activated carbon based on Indonesian Standard (SNI No. 06-3730-1995) at 15%.

3.1.2. Effect of Carbonization Temperature and Carbonization Time on Ash Content. Ash content shows the amount of inorganic substituents present in the carbon [21]. The effect of carbonization temperature and carbonization time on ash content of activated carbon from rice husk is shown in Fig. 2.

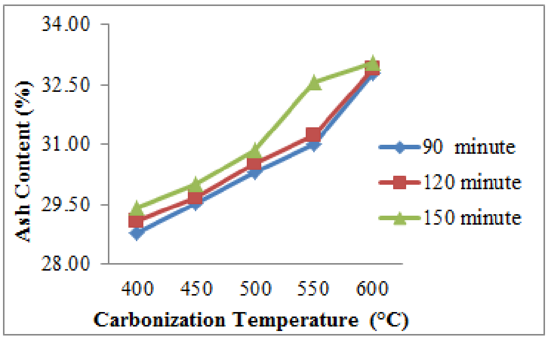

Figure 2. Effect of Carbonization Temperature and Carbonization Time on Ash Content

From Fig. 2, explained higher carbonization temperature and carbonization time followed with increased ash content.

High ash content is undesirable because it reduces the mechanical strength and adsorption capacity of produced activated carbon. Minimum ash content of activated carbon makes it highly favorable for commercial applications [10]. All sample ash content did not conform to Indonesian Standard (SNI No. 06-3730-1995) at 10%.

3.1.3. Effect of Carbonization Temperature and Carbonization Time on Volatile Matter Content. The effect of carbonization temperature and carbonization time on volatile matter content of activated carbon from rice husk is shown in Fig. 3.

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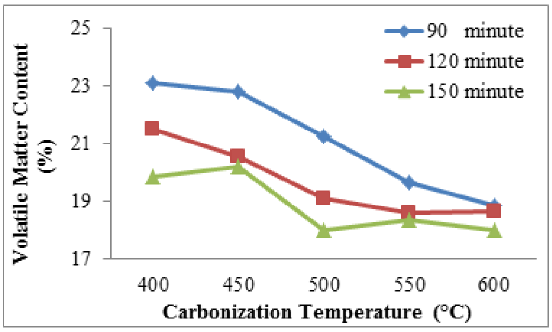

Figure 3. Effect of Carbonization Temperature and Carbonization Time on Volatile Matter Content

From Fig. 3, explained higher carbonization temperature and carbonization time decreased volatile matter content of activated carbon.

The amount of volatile matter corresponds to compounds that have not evaporated during carbonization, but evaporates at 950 °C [20]. Volatile matter is due to the presence of organic compounds present in the raw material [21]. All sample volatile matter content suitable the standards for activated carbon based on Indonesian Standard (SNI No. 06-3730-1995) at 25%.

3.1.4. Effect of Carbonization Temperature and Carbonization Time on Fixed Carbon. The effect of carbonization temperature and carbonization time on fixed carbon of activated carbon from rice husk is shown in Fig. 4.

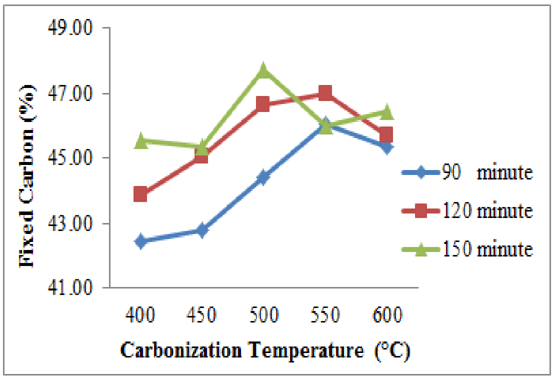

Figure 4. Effect of Carbonization Temperature and Carbonization Time on Fixed Carbon

From Fig. 4, explained higher carbonization temperature and carbonization time followed with increased fixed carbon.

Fixed carbon is the amount of pure carbon contained in carbon. The determination of fixed carbon aims to determine the carbon content after carbonization [20].

The highest fixed carbon obtained 47.75% at temperature of 500 ° C for 150 minute. This condition shows the optimum carbonization of activated carbon from rice husk. All sample fixed carbon did not conform to Indonesian Standard (SNI No. 06-3730-1995) at 65%.

3.2. Analysis of Scanning Electron Microscope (SEM)

To characterize the surface structure and morphology of untreated, treated rice husk and treated rice husk after adsorption of car battery wastewater, SEM analysis was carried out scanning electron microscope.

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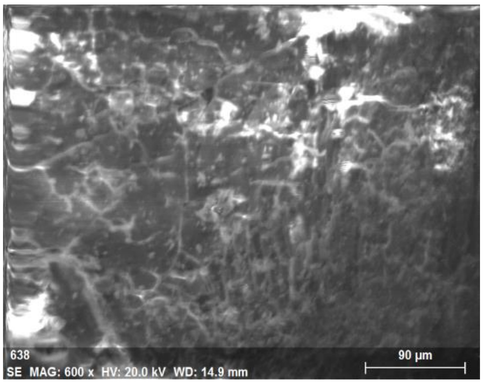

Figure 5. SEM of Rice husk

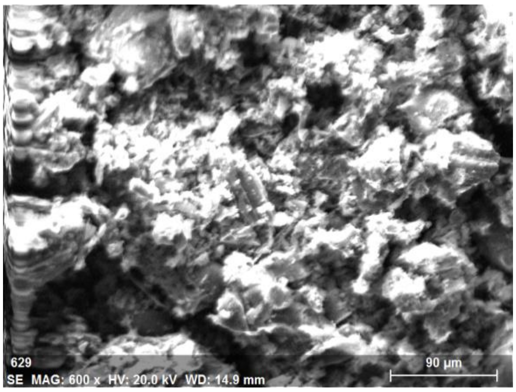

Figure 6. SEM of Rice Husk After Carbonization

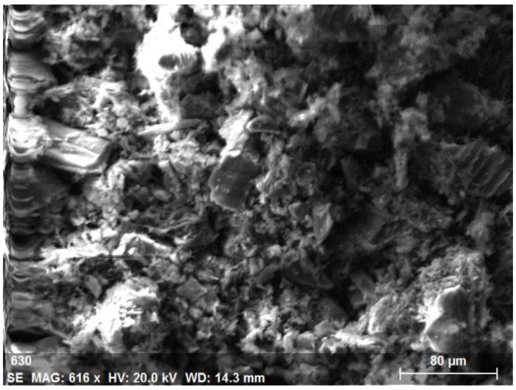

Figure 7. SEM of Activated Carbon

The SEM images of raw rice husk, rice husk after carbonization, and activated carbon are shown in the Fig. 5, 6 and 7. Fig. 5, explained the result of the analysis of raw rice husks which the structures pore cannot be seen because of the absence of treatment the rice husk. Silica present on the outer surface of rice husks in the form of silicon-cellulose membrane acts as a natural protective layer against termites and other microbial attack on the paddy [22].

While Fig. 6, explained rice husk after carbonization seen distribution pores. Result of activated carbon in Fig. 7, explained surface pores of activated carbon is amorphous. Surface morphology of rice husk without activation changed significantly after activated with sodium carbonate pores and cavities [23].

Na_2CO_3 is reduced to metallic sodium by carbon during the carbonization process according to the following reaction [3].

$$Na_2CO_3 + 2C \longrightarrow 2Na + 3CO \qquad (7)$$

The sodium metal atoms occurred during the activation stage could intercalate into the carbon structure and widen the existing pores and create new porosities [3].

3.3. Analysis of Energy Dispersive Spectroscopy (EDS)

Energy Dispersive Spectroscopy (EDS) of the samples were obtained by mounting the sample on gold and by using scanning electron microscope with energy dispersive spectrum for elemental analysis.

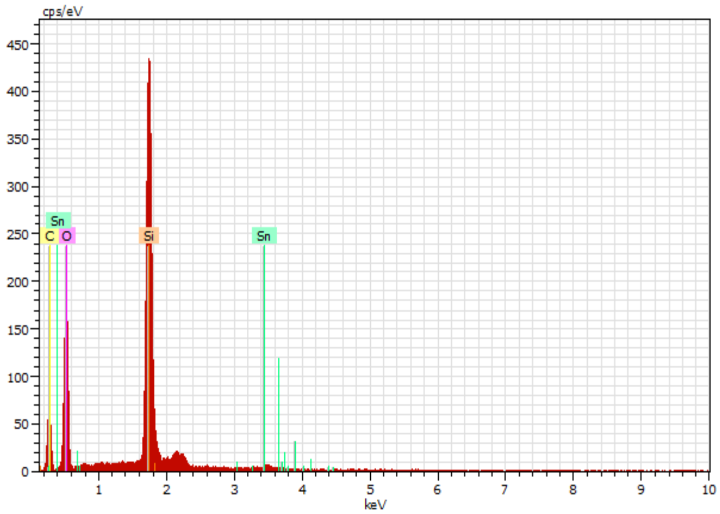

Figure 8. EDS of Rice Husk

Table 4. EDS of Rice Husk

Spectrum: SEKAMPADI

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

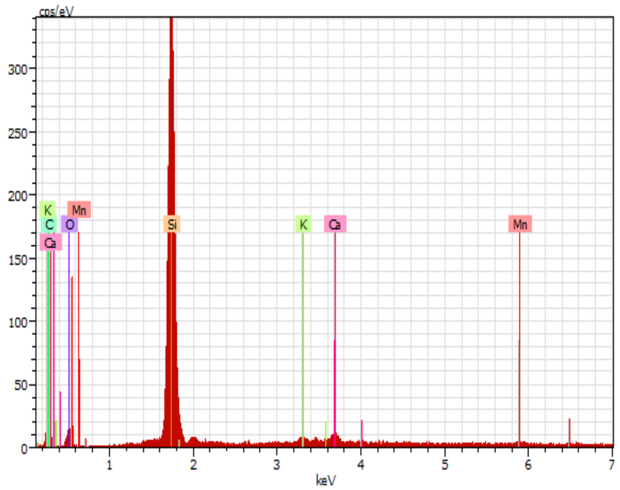

Figure 9. EDS of Rice Husk After Carbonization

Table 5. EDS of Rice Husk After Carbonization

Spectrum: KarbonFK500

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

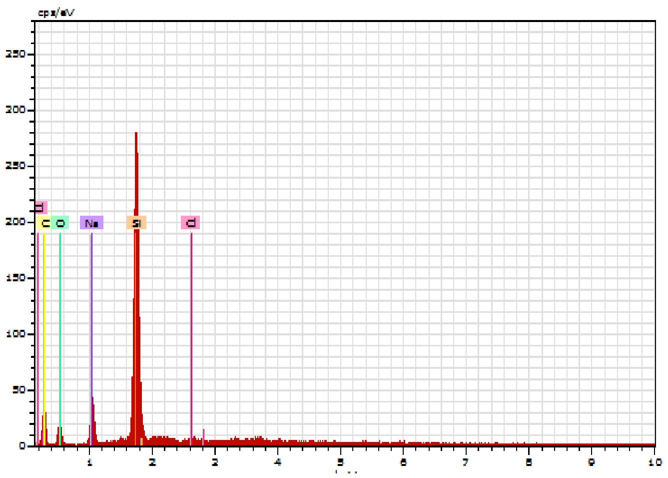

Figure 10. EDS of Activated Carbon

Table 6. EDS of Activated Carbon

Spectrum: Na2CO3karbonactFK

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]
C	6	K-series	21.09	47.58	61.93
Si	14	K-series	8.88	20.03	11.15
O	8	K-series	7.52	16.97	16.58
Na	11	K-series	6.57	14.82	10.08
Cl	17	K-series	0.27	0.60	0.27
		Total:	44.33	100.00	100.00

The difference between carbon and fixed carbon content because carbon content includes all carbon present in the sample, both fixed and removed in the volatile compounds; that is why carbon content is higher that fixed carbon content [10].

EDS results showed that the main elements of the rice husk activated carbon is carbon (C). Fig. 8, 9 and 10 and table 4, 5 and 6 show that rice husk has some chemical elements that consisted of 45.84% O; 42.08% C; 11.96% Si; and 0.11% Sn. Rice husk after carbonization has some chemical elements containing of 56.57% C; 26.72% Si; 15.37% O; 0.67% Ca; 0.49% K and 0.19% Mn. Activated carbon have some chemical elements containing of 61.93% C; 16.58% O; 11.15% Si; 10.08% Na and 0,27% Cl.

3.4. Adsorption Of Lead From Car Battery Wastewater

According government regulation No.82 2011 of the Metal lead content at water around 0, 03 mg/L, while Decision Minister of the Environment No.51 2004 about effluents standards for industrial activities with maximum lead content is 0, 1 mg/L [24]. Current USEPA drinking water standard for lead is 0.015 mg/l [11].

Sodium carbonate modified of activated carbon from rice husk to removed many ions [23]. Activated carbon is the optimum condition is used to test their effectiveness in reducing the concentration's level of heavy metals in car battery wastewater to reduce the content (lead) Pb. The initial concentration of wastewater is 10,3437 mg/l, while the final concentration of wastewater is 4,6706 mg/l. Adsorption capacity obtained at 0, 6007 mg/g with a percentage of percentage removal at 58.08%.

4. Conclusions

The results of this study show that it is feasible to prepare activated carbons from rice husk by chemical activation. Activation with Na_2CO_3 is not only a low cost biomass with high adsorption capacity. The optimum condition got best obtained at a temperature of 500 °C for 150 minute with the characteristics of 3.35% moisture, 30.86% ash, 18.04% volatile matter. Based on EDS results showed that the main elements of the rice husk activated carbon is carbon (C). Carbon content of rice husk 42.08%; rice husk after carbonization containing of 56.57%; activated carbon containing of 61.93% C. Furthermore, adsorption of lead from car battery wastewater. The adsorption capacity obtained was 0.56731 mg/g with a percentage removal at 54.85%.

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