Coal Fly Ash as Adsorbent in Removing Organic Compounds (COD) From Tanah Tinggi Wastewater Treatment Installation in Tangerang City

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ABSTRACT

Coal is a combustible organic mineral; the ash produced from burning coal is fly ash and bottom ash. This study aims to determine the process of treating fly ash waste from coal combustion by activating and characterizing it as an adsorbent and to obtain the best type of adsorbent with a concentration of coal fly ash as an adsorbent in removing organic compounds COD so that it meets the standards. Quality by accordance with the Regulation of the Minister of Environment and Forestry Number 68 of 2016 concerning Domestic Wastewater Quality Standards. The research will be carried out with 2 (two) processes, namely the process of making adsorbents and testing the application of fly ash adsorbents with variations in the concentration of sulfuric acid (H₂SO₄) 2.5%, 5%, and 10% and variations in stirring time of 60, 90, 120 and 150 minutes, then analyzed the COD (Chemical Oxygen Demand) content so that it meets the quality standards that have been set. The results showed that the fly ash content of coal has the potential to be used as an adsorbent because of the high SiO₂ content of 35.8% and the Al₂O₃ content of 17.0%. Results The initial concentration of COD was 404 mg/l. The final concentration of COD for various stirring times with various H₂SO₄ activation was 11 mg/l with a stirring time of 150 minutes. Optimum conditions of removal efficiency (%) COD for variation of stirring time with various H_2SO_4 activation obtained 35.73%, R^2 value = 0.9891, and the linear regression equation is y = 0.206x - 4.864 with the value of y is COD efficiency removal (%) and x is stirring time (minutes).

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INTRODUCTION*

Process burning coal to produce power in the industry will produce combustion residue which is called fly ash as well as bottom ash which is hazardous and toxic waste so it is very dangerous if it pollutes the air surrounding or ambient air (Lasryza and Dyah, 2012), handling fly ash alone generally only stacked in the area around the industry or disposed of in a landfill. Handling fly ash that is less than optimum can be harmful to the surrounding environment, such as Fly ash blown by the wind can interfere with breathing and naturally will cause pollution air. The more increase usage of coal, so the burden environment also will the more heavy and need to be anticipated the look for

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utilization by optimal so as could reduce the level of pollution environment (Irawan et al, 2015).

Fly ash is fly ash left over from coal combustion which amounts to about 80-90% of the total ash, while the amount of bottom ash is only around 10%. Fly ash coal contain SiO₂ (52.0%), Al₂O₃ (31.9%), Fe₂O₃ (5%), CaO(3%) and MgO (5%) (Kutchko and Kim, 2006). Besides that fly ash also contain mineral minor other as magnesium, sulfur, sodium, potassium, and carbon. The presence of components silica and alumina allow ash kite to could synthesize and become material which a structure similar to zeolite or known as zeolite like materials (ZLM). The porous structure of the zeolite is a property that can be utilized as a material adsorbent (Mufrodi et al, 2010).

In accordance with Government Regulation of the Republic of Indonesia Number 22 Year 2021 about maintenance Protection and Management

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Environment Life fly ash which sourced from process coal combustion in Stocker Boilers and/or Industrial furnaces including types of toxic and hazardous waste and proper management is required good and right so that safe for health and the environment life.

Based on the level of population density and the rate of growth every year increase in Indonesia especially in City Tangerang, many activities are carried out by residents such as bathing, washing clothes, washing dishes, etc. all of these activities produce waste called water in household waste. In the Ministerial Regulation accordance with Environment Life and Forestry Number 68 Year 2016 about raw Quality Domestic Wastewater, the COD parameter is one of the parameters that must fulfill the threshold limit with a rated maximum 100 mg/l. Because it is necessary to do research on fly ash processing as an adsorbent, characterization, and its application in the removal of wastewater parameters one of which is the COD parameter by utilizing fly ash coal as adsorbent so that Fulfill raw quality water waste domestic.

EXPERIMENTAL METHOD

Equipment and materials

The materials that will be used in this research consist of the main raw materials and auxiliary materials. The main raw materials to be used are coal fly ash and domestic liquid waste. Coal fly ash will be used is coal fly ash sourced from process burning coal combustion in the Stocker Boiler and/or furnace of one of the industries in Tangerang City, PT. Daya Cipta Kemasindo, while waste liquid domestic that will be used originated from Installation Tanah Tinggi Tangerang City Wastewater Treatment. Auxiliary materials used are ingredient chemicals in the form of H₂SO₄ 2.5%, 5%, and 10% for activating coal fly ash. Equipment used in the study this including XRF (X-Ray Fluorescence) Spectrometer, flat bottom boiling flask, hotplate magnetic stirrer, oven, cup, paper filter, glass beaker, digital scale, bottle glass, glass measuring, thermometer, pH meter, equates, measuring pipette, burette, Erlenmeyer.

Determination Initial COD Concentration (mg/l) *fly ash* is analyzed in the laboratory using an S spectrophotometer according to SNI 6989.2:2019 to determine the initial concentration of COD (mg/l).

Making adsorbent

fly ash adsorbent is made by characterizing fly ash coal using an XRF (X-Ray Fluorescence) Spectrometer and activating fly ash by adding a solution of H_2SO_4 2.5%, 5%, and 10% as much as 100 ml into 20 grams of fly ash in a flat bottom

boiling flask then refluxed at 95°C for 120 minutes with the help of a hotplate magnetic stirrer, stirring at 150 rpm. Then fly ash was filtered using filter paper and washed with distilled water several times to reduce its acidity (until the pH is neutral). Fly ash was dried in an oven at 110°C for 1 hour. The resulting adsorbent was tested for characterization using an XRF (X-Ray Fluorescence) Spectrometer. (Marisa, 2017).

Application Test Coal *Fly Ash* Adsorbent in Waste Liquid Domestic

The application test of coal fly ash to determine the optimum conditions was carried out by stirring between the adsorbent and liquid waste into a stirred tank with a fixed variable speed of 150 rpm, the adsorbent diameter of 0.09 mm, and waste volume of 500 ml with variations in stirring time (60, 90, 120 and 150 minutes), then the results were filtered and analyzed for their COD content (Ari, 2013).

Analysis Method

Product data analysis was carried out in an environmental laboratory to determine the COD concentration after research was carried out using an S spectrophotometer according to SNI 6989.2:2019 . Furthermore, data processing is carried out using optimization analysis to determine the best (optimal) COD removal percentage value. COD removal Analysis can be calculated with overall efficiency. Percent elimination was used for determining water quality with compare initial COD concentration with COD concentration after the adsorption process (Kasam et al., 2005). The equation of removal efficiency percent:

efficiency (%) =
$$\frac{Co - Ce}{Ce} X 100\%$$

Description:

Co = Concentration initial (mg/l) Ce = Concentration end (mg/l)

RESULTS AND DISCUSSION Concentration Results (mg/l)

To get the results of the initial COD concentration of domestic wastewater, samples were taken at the inlet of the Tanah Tinggi Tangerang City Wastewater Treatment Plant (IPAL), and further analysis was carried out in the laboratory, from the results of the Test Result Report at the Inlet of the Tanah Tinggi Tangerang City Wastewater Treatment Plant (IPAL) obtained a pH concentration of 6.51 and a COD concentration of 404 mg/l, and this has exceeded the quality standard stipulated in

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accordance with the Ministerial Regulation Environment Life and Forestry Number 68 Year 2016 about raw Quality Domestic Wastewater where the threshold is 100 mg/l.

Coal Fly Ash Characterization

From the Fly result, Coal Ash characterization before activated use solution sour sulfate then conducted the analysis using XRF (X-Ray Fluorescence) analysis obtained that SiO₂ content including high namely 35.8% and the content of Al₂O₃ by 17.0% so that Fly Ash Coal potential for the made adsorbent. Content biggest Fly ash Coal is Si, Al, Fe, Ca, and Na, while element oxide also applies content biggest present in SiO₂, Al₂O₃, Fe₂O₃, CaO, and Na₂O. elements that will affect the next process from the utilization of Coal Fly Ash, such as elements of Si and Al that function for utilization of Coal Fly Ash as a Zeolite that is a perforated material having structure crystal Aluminosilicate and take advantage of as adsorbent or catalyst, other than used as Zeolite Fly Ash Coal can be utilized as mixture ingredient building like cement or Concrete brick where required elements such as Ca (Lasryza and Diah, 2012). Activation of Coal Fly Ash is performed with the use of Sour Sulfate (H₂SO₄) with variations of 2.5%, 5% and 10%, treatment activation of the Fly Ash of the Coal could increase SiO₂ level the more approach specification adsorbent with high levels of tin. The results of the characterization of Fly Ash Coal before and after conducted Activation could be seen in Table 1 as follows:

No	Variation of H ₂ SO ₄ Concentration	Time (Minutes)	Concentration Results (%)				
			SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O
1	No Activation*)	-	35.8	17.0	2.87	0.67	0.16
2	2.5	120	37.4	5.54	1.95	0.26	0.15
3	5	120	41.7	4.20	0.66	0.25	0.18
4	10	120	37.1	3.80	0.67	0.18	0.20

41

40 39 38

37

35 34

33 32

No Activation

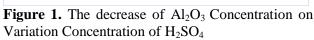
SiO2 Concentration (%)

41,7

37,1

10

Table 1. Test Results Fly Ash Coal



H2SO4 Concentration

37,4

Table 1 above could see the SiO_2 level seen increases for every increase in the concentration of H_2SO_4 added to the purification process, with the

increase obtained that SiO_2 increases along enhancement concentration of H_2SO_4 used for purifying Fly Ash Coal.

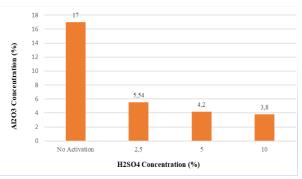


Figure 2. The decrease of Al_2O_3 Concentration on Variation Concentration of H_2SO_4

In Figure 2 can see at addition concentration of $H_2 SO_4$ occur drop in concentration of Al_2O_3 , this caused at the time Fly Ash Coal to reflux with the solution $H_2SO_4 Al_2O_3$ content in Fly Ash Coal will dissolve with reaction as follows:

$$Al_2O_3 + H_2SO_4 \longrightarrow Al_2(SO_4)_3 + H_2O$$

(Vogel, 1985)

Temporary SiO_2 concentration in Coal Fly Ash is increasing increase consequence decrease concentration Al_2O_3 , while SiO_2 is not soluble by H_2 SO_4 (Vogel, 1985).

Application test of the adsorbent

The application test is used to determine the optimum stirring time, the optimum conditions are determined based on the efficiency largest COD removal. As for the conditions for general application test optimization, this is to use coal fly ash as an adsorbent with variation time stirring (60, 90, 120, and 150 minutes). Test app optimization was carried out on the volume of waste liquid domestic 500 ml, with an adsorbent diameter of 0.09 mm and a weight/mass of 3 g, and round stirring at 150 rpm. Research results are arranged in form of tables and graphs which influence time stirring to COD concentration and removal.

Application test of the optimum adsorbent without H_2SO_4 Activation

Application test of the optimum adsorbent coal fly ash without activation of H_2SO_4 was conducted for knowing how many Final COD concentration (mg/l) and efficiency COD removal with waste volume liquid domestic 500 ml, with an adsorbent diameter of 0.09 mm and a weight/mass of 3 g and round stirring 150 rpm and variations time stirring on application test this are 60, 90, 120 and 150 minutes. Application test results adsorbent variation time stirring could see in table 2, figure 3, and figure 4.

Table 2. Final Concentration and Efficiency CODremoval on variations time stirring withoutactivation of H_2SO_4

No	Mixing Time Variation (Minutes)	pН	COD concentration (mg/l)	COD Removal Efficiency (5)
1	60	7.74	25	15,16
2	90	7.70	22	17.36
3	120	7.81	20	19,20
4	150	7.85	17	22.76

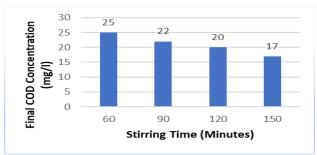


Figure 3. The Comparison Final COD Concentration (mg/l) for variation stirring time without activation of H_2SO_4

Figure 3 above seen that occur drop in COD concentration for all variation stirring without activation of H₂SO₄. For time stirring 60 minutes occur drop COD concentration of concentration initial COD 404 mg/l to concentration final COD 25 mg/l, for time 90 min stirring occur drop to 22 mg/l, for time stirring 120 minutes to occur drop to 20 mg/l, while time stirring 150 minutes occur drop COD concentration from 404 mg/l to 17 mg/l and this is drop greatest COD concentration. This thing strengthens the statement time stirring is something very decisive thing in the adsorption process, the longer the time stirring allows diffusion and attachment processes molecule adsorbate in progress better and the concentration of substances organic will drop (Reynolds, 1982).

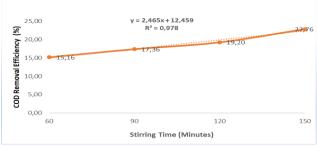


Figure 4. The Comparison Removal Efficiency of COD (%) for variation stirring time without activation of H_2SO_4

In Figure 4 above could see for variation of time stirring 60 minutes to occur drop concentration with an efficiency COD removal of 15.16%, for time 90 min stirring efficiency COD removal is 17.36%, and for time stirring 120 minutes to occur efficiency COD removal is 19.20%, while efficiency COD removal on time stirring 150 minutes by 22.76%. The study previously also stated that time mixing affects an adsorption process, the longer the time stirring so the percentage of COD removal is getting increases (Ari, 2013).

Based on Figure 4 above is also appropriate with results calculation COD removal obtained equality linear regression y = 2,465x + 12,459, with the value of y is efficiency removal (%) and x is time stirring (minutes), as for value $R^2 = 0.978$ p this showing existence correlation between y and x, where the longer the time stirring, then the more high value too efficiency removal (%).

Application test of the optimum adsorbent with activation of $H_2SO_4 2.5\%$

The result of Application Test of optimum adsorbent coal fly ash with activation of H2SO4 2.5% is done for knowing how many Final COD concentration (mg/l) and efficiency COD removal with waste volume liquid domestic 500 ml, with an adsorbent diameter of 0.09 mm and a weight/mass of 3 g and round stirring 150 rpm and variations time stirring on application test this are 60, 90, 120 and 150 minutes. Application test results adsorbent variation time stirring could see in table 3, figure 5, and figure 6 below this.

Table 3. Final Concentration and Efficiency COD removal on various variation time stirring with activation of $H_2SO_4 2.5\%$

No	Mixing Time Variation (Minutes)	рН	COD concentration (mg/l)	COD Removal Efficiency (%)
1	60	7.71	37	9.92
2	90	6.59	35	10.54
3	120	6.46	28	13.43
4	150	6.39	15	25.93

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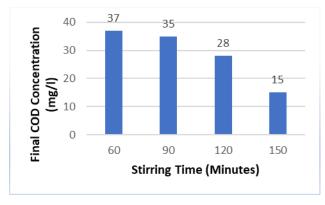


Figure 5. The comparison Final COD Concentration (mg/l) for variation stirring time with activation of $H_2SO_4 2.5\%$

In Figure 5 above see that occur drop COD concentration for all variation stirring with activation of H₂SO₄ 2.5%. For time stirring 60 minutes occur drop COD concentration of concentration initial COD 404 mg/l to concentration final COD 37 mg/l, for time 90 min stirring occur drop to 35 mg/l, for time stirring 120 minutes occur drop be 28 mg/l, while time stirring 150 minutes occur drop COD concentration from 404 mg/l to 15 mg/l and this is drop greatest COD concentration. This thing strengthens the statement time stirring is something very decisive thing in the adsorption process, the longer the time stirring allow diffusion and attachment processes molecule adsorbate in progress better concentration of substances organic will drop (Reynolds, 1982).

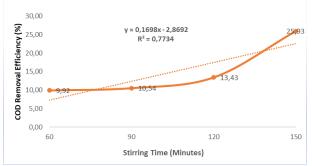


Figure 6. The Comparison Removal Efficiency of COD (%) for variation stirring time with activation of $H_2SO_4 2.5\%$

In Figure 6 can see for variation time stirring 60 minutes occur drop concentration with efficiency COD removal of 9.92%, for time 90 min stirring efficiency COD removal of 10.54%, and for time stirring 120 minutes occur efficiency COD removal is 13.43%, while efficiency COD removal on time stirring 150 minutes by 25.93%. Study previously also stated that time mixing really affects an adsorption process, the longer the time stirring so

percentage COD removal is getting increase. (Ari, 2013).

Based on Figure 6 above is also appropriate with results calculation COD removal obtained equality linear regression y = 0.1698x - 2.8692, with the value of y is efficiency removal (%) and x is time stirring (minutes), as for value $R^2 = 0.7734$ p this showing existence correlation between y and x, where the longer the time stirring, then the more high value too efficiency removal (%).

Application test of the optimum adsorbent with activation of $H_2SO_45\%$

The result of the Application Test of optimum adsorbent coal fly ash with activation of H2SO4 5% done for knowing how many Final COD concentration (mg/l) and efficiency COD removal with waste volume liquid domestic 500 ml, with an adsorbent diameter of 0.09 mm and a weight/mass of 3 g and round stirring 150 rpm and variations time stirring on application test this are 60, 90, 120 and 150 minutes. Application test results adsorbent variation time stirring could see in table 4, figure 7, and figure 8 below this.

Table 4. Final Concentration and Efficiency CODremoval on various variation time stirring withactivation of $H_2SO_45\%$

No	Mixing Time Variation (Minutes)	рН	COD concentration (mg/l)	COD Removal Efficiency (%)	
1	60	7.62	32	11.63	
2	90	6.54	31	12.03	
3	120	6.65	23	16.57	
4	150	6.58	14	27.86	

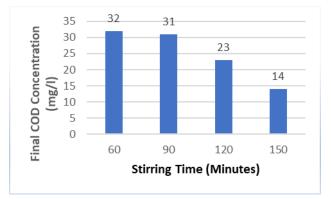


Figure 7. The comparison Final COD Concentration (mg/l) for variation stirring time with activation of $H_2SO_45\%$

In Figure 7 above see that occur drop COD concentration for all variation stirring time with activation of $H_2SO_45\%$. For time stirring 60 minutes occur drop COD concentration of concentration

initial COD 404 mg/l to concentration final COD 32 mg/l, for time 90 min stirring occur drop to 31 mg/l, for time stirring 120 minutes occur drop be 23 mg/l, while time stirring 150 minutes occur drop COD concentration from 404 mg/l to 14 mg/l and this is drop greatest COD concentration. This thing strengthens the statement time stirring is something very decisive thing in the adsorption process, the more long time stirring allow diffusion and attachment processes molecule adsorbate in progress better concentration of substances organic will drop (Reynolds, 1982).

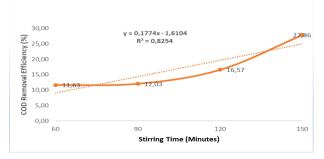


Figure 8. The Comparison Removal Efficiency of COD (%) for variation stirring time with activation of $H_2SO_45\%$

In figure 8 can see for variation time stirring 60 minutes occur drop concentration with efficiency COD removal of 11.63%, for time 90 min stirring efficiency COD removal of 12.03%, and for time stirring 120 minutes occur efficiency COD removal is 16.57%, while efficiency COD removal on time stirring 150 minutes by 27.86%. Study previously also stated that time mixing really affects an adsorption process, the longer the time stirring so percentage COD removal is getting increase. (Ari, 2013). Based on Figure 8 above is also appropriate with results calculation COD removal obtained equality linear regression y = 0.1774x - 1.6104, with the value of y is efficiency removal (%) and x is time stirring (minutes), as for R value² = 0.8254 p this showing existence correlation between y and x, where the longer the time stirring, then the more high value too efficiency removal (%).

Application test of the optimum adsorbent with activation of $H_2SO_4 10\%$

Test app optimization adsorbent coal fly ash with activation of H_2SO_4 10% is done for knowing how many Final COD concentration (mg/l) and efficiency COD removal with waste volume liquid domestic 500 ml, with an adsorbent diameter of 0.09 mm and a weight/mass of 3 g and round stirring 150 rpm and variations time stirring on application test this are 60, 90, 120 and 150 minutes . Application test results adsorbent variation time stirring could seen in table 5, figure 9 and figure 10 below this.

Table 5. Final Concentration and Efficiency COD removal on various variation time stirring with activation of $H_2SO_4 10\%$

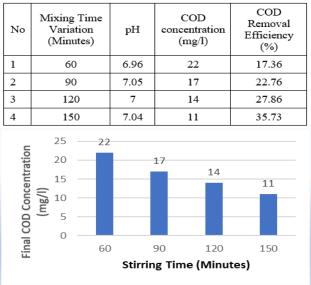


Figure 9. The comparison Final COD Concentration (mg/l) for variation stirring time with activation of H_2SO_4 10%

In Figure 9 above seen that occur drop in COD concentration for all variations stirring with activation of H2SO4 10%. For time stirring 60 minutes occur drop COD concentration of concentration initial COD 404 mg/l to concentration final COD 22 mg/l, for time 90 min stirring occur drop to 17 mg/l, for time stirring 120 minutes to occur drop to 14 mg/l, while time stirring 150 minutes occur drop COD concentration from 404 mg/l to 11 mg/l and this is drop greatest COD concentration. This thing strengthens the statement time stirring is something very decisive thing in the adsorption process, the longer the time stirring allows diffusion and attachment processes molecule adsorbate in progress better concentration of substances organic will drop (Reynolds, 1982).

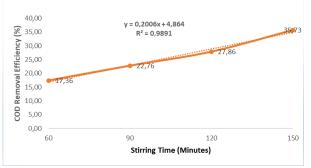


Figure 10. The Comparison Removal Efficiency of COD (%) for variation stirring time with activation of $H_2SO_4 10\%$

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In Figure 10 can see for variation time stirring 60 minutes occur drop concentration with efficiency COD removal of 17.36%, for time 90 min stirring efficiency COD removal is 22.76%, and for time stirring 120 minutes occur efficiency COD removal is 27.86%, while efficiency COD removal on time stirring 150 minutes by 35.73%. Study previously also stated that time mixing really affects an adsorption process, the longer the time stirring so percentage COD removal is getting increase (Ari, 2013).

Based on Figure 10 above is also appropriate with results calculation COD removal obtained equality linear regression y = 0.206x + 4.864, with the value of y is efficiency removal (%) and x is time stirring (minutes), as for value $R^2 = 0.9891$ p this showing existence correlation between y and x, where the longer the time stirring, then the more high value too efficiency removal (%).

From the results of data processing as a whole, it was found that the most optimum condition of COD removal efficiency for stirring time without H_2SO_4 activation was 22.76% with a stirring time of 150 minutes. Meanwhile, for the most optimum condition, the COD removal efficiency with stirring time with H_2SO_4 activation is 35.73 $_{\%}$, integrating findings from research into existing knowledge sets and compiling new theories or modifying existing theories.

CONCLUSION

Based on the data and discussion obtained, the research about the utilization of coal fly ash as an adsorbent in elimination compound organic COD from Wastewater Treatment Installation Tanah Tinggi Tangerang City:

- a. The characterization of coal fly ash got that SiO_2 content high namely 35.8% and the content of Al_2O_3 by 17.0% so that Fly Ash Coal potential for adsorbent;
- b. The initial concentration of COD is 404 mg/l;
- c. The final concentration of COD for variation time stirring (60, 90, 120 and 150 minutes) with activation of H₂SO₄ (2.5, 5, and 10%) obtained 11 mg/l with time 150 minutes of stirring, this showing adsorbent coal fly ash _ could lower wastewater COD concentration domestic so that fulfill raw quality in accordance Regulation of the Minister of Environment and Forestry Number P.68/Menlhk/Setjen/Kum.1/8/2016 concerning Domestic Wastewater Quality Standards;

d. The optimum condition of removing efficiency (%) for variation time stirring (60, 90, 120 and 150 minutes) with activation of H $_2$ SO $_4$ (2.5, 5, and 10%) obtained 35.73%, the value of R² = 0.9891 and the linear regression equation is y = 0.206x - 4.864 with time stirring 150 minutes.

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