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The electrochemical properties of water hyacinth-derived activated carbon

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Abstract

The water hyacinth (WH)-based activated carbon (WHac) has been prepared by an acid treatment, pyrolytic carbonization, and alkali activation processes for using as electrode materials of electrochemical energy storage devices. The pyrolytic carbonization process was performed at a variety of temperature (600, 700, and 800°C) for 2 h. The ash-prepared samples were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET). The benefits of activated carbon with large uniform surface area leading to maximum specific capacitance of 98.3 $F \cdot g^{-1}$ and good cycling stability. Attributed to low-cost make the water hyacinth activated carbon has the potential for use as electrode materials of energy storage devices. Moreover, the decreasing of water hyacinths maintains environmental equilibrium and is sustainable.

1. Introduction

Water hyacinth is a plant that lives in general water sources and can propagate quickly, especially during the rainy season. Particularly, if it is a water source in the water hyacinth community, it can grow by being able to absorb the nutrients that cause wastewater by relying on chemicals used in the daily life of the community such as detergents and fertilizers, which are plant nutrients, especially great nutrients for water hyacinths. However, if there is too much water hyacinth, it will result in blocking the water way, blocking the drainage of the sluice. In addition, it also damages ecosystems and affects aquatic life, oxygen deprive and death of underwater animals, as well as blocking sunlight for the photosynthesis of underwater plants, causing them to rot and die, thus easily rotten water, resulting in the destruction of ecosystems in that water source. Energy is related to the livelihood of people all over the world. In addition, the demand for energy consumption is likely to increase in many countries. Thailand is a country that is in a developing stage and continuedly industrial growth, so there are many attempts to invent and develop new alternative energy sources. The most obvious and widely used energy storage devices are high-efficiency batteries and supercharged electrochemical capacitors. Currently, such energy storage is low efficiency, expensive, not durable, and not enough to meet the current demands with the low short lifespan of keeping energy per unit weight of energy storage, creating problems with difficulty to destroy as wastes and pollution to the environment. Supercapacitors are electrochemical energy storage devices that have quick charging and discharging rates, high power densities, long cycle lives, and consistent performance. They can be used in a variety of electronic equipment, including hybrid cars, notebook computers, and mobile phones [1]. The supercapacitor can be divided into two types: carbon-based electrical double-layer capacitors (EDLCs), pseudocapacitors [2,3] and hybrid capacitor [4]. Among several biomass as precursor of lignocellulose for activated carbon (AC). Many biomasses derived AC such as bamboo [5], wood, water hyacinth [6,7], sensitive plant [8], banana peel [9], rick husk [10], nipa palm husk [11], soyabean [12], sugarcane waste [13] and mangosteen peel [18]. The electrical double-layer capacitor (EDLC), a type of supercapacitor that the AC electrode stores charge based on the buildup of electrolyte ions on the surface of a highly porous carbon [18,19]. From this perspective, the pores of carbon-based electrodes act as pathways for the transfer of electrolyte ions. As a result, the specific surface area and porous structure are crucial factors in determining the electrochemical performance of carbon-based electrode materials [20]. AC are used applications for energy storage, because of their high surface, performance stability, friendly to the environment and low cost [14]. The water hyacinth contains a high concentration of lignocellulose biomass making it a potential candidate for use as a carbon source [7,22]. The activated carbon from the water hyacinth exhibited excellent specific surface area, high specific capacitance, and good cycle stability [15,23]. Thermo-chemical conversion of water hyacinth to biochar is thus a viable technique for enhancing energy and environmental sustainability [24]. Above mentioned the water hyacinth is therefore an interesting aquatic plant to develop technology to transform water hyacinth into high-quality materials with emphasizing on the process of converting water hyacinths into carbon to become a high-quality activated carbon material, porous, hygroscopic, and high organic matter and further developed into carbon for the manufacture of supercapacitor electrodes. Therefore, in this research, the aim synthesized the water hyacinth charcoal by thermal method at different temperatures, then studied its characteristics and study of electrochemical properties of water hyacinth charcoal.

2. Experimental

In this research, the objective of this research was to study the synthesis of activated derived-carbon from water hyacinth by thermal method to find techniques to synthesize and improve electrochemical properties of this water hyacinth biomass carbon for increased electric capacity. The research team has conducted research as follows:

2.1 Preparation of activated carbon from water hyacinth (WHac)

Water hyacinth was prepared by washing with clean water thoroughly and cut into small pieces. Small pieces were dried at 80°C for 24 h, then grinded thoroughly. Water hyacinth powder was soaked into hydrochloric acid at 0.25 M concentration for 12 h, then rinsed with DI water until the pH changed to 7, then dried at 80°C for 24 h. After that, it was burned out at 450°C for 2 h, after which the temperature was increased into 800°C for 2 h. Carbon from water hyacinth (WHc) was soaked in potassium hydroxide for 1 h. Prepared soaked carbon from water hyacinth with potassium hydroxide was calcined at 600, 700 and 800°C for 2 h under Ar atmosphere, then denoted as WHac600, WHac700, and WHac800, respectively. Finally, water hyacinth activated carbon was soaked with 0.25 M hydrochloric acid for 12 h and washed out with DI water until the pH changed to 7.

2.2 Characterization

The sample powder to study the specific characteristics: the crystal structure by X-ray diffraction (X-ray diffraction; XRD) (D2, Bruker, Germany). The surface characteristics and microscopic morphology of the samples were studied by scanning electron microscope (SEM). The samples were degassed at 300°C for 24 h. The specific surface area and pore size distribution were measured at 77 K by using N_2 adsorption/desorption techniques (BELSORP Mini II).

Figure 1. The scheme of the preparation process.

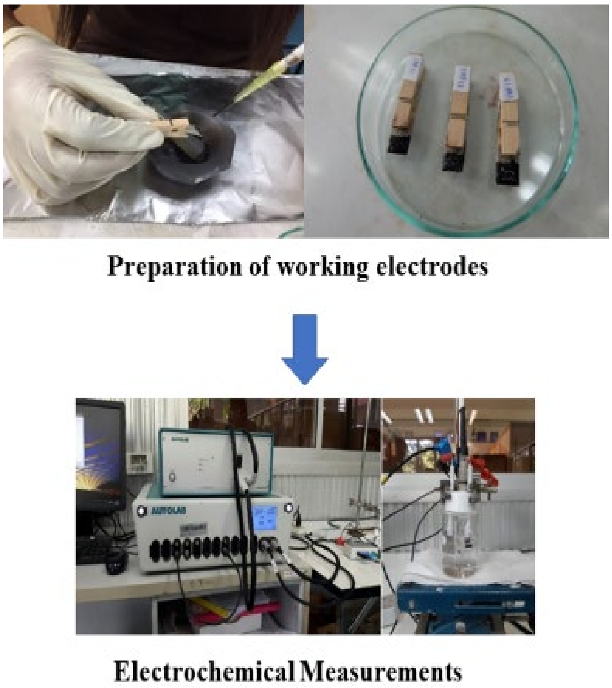

Figure 2. The scheme of the preparation working electrode and electrochemical measurement.

2.3 Preparation of working electrodes

The researcher mixed carbon/activated carbon powder with Carbon black and Polyvinylidene fluoride (PVDF) with a ratio of 8: 1: 1, which dissolved in N-Methyl-2-pyrrolidone (NMP) 200 µL, and ground to homogeneous slurry. The slurry was then dripped onto nickel foam in an area of 1x1 cm and dried at 80°C for 24 h. It was compacted into thin sheets and then immersed in KOH for 24 h.

2.4 Electrochemical Measurements

The electrochemical properties were measured in a three-electrode system with the following techniques: Cyclic Voltammetry (CV), Galvanostatic Charge – Discharge (GCD) and Electrochemical impedance spectroscopy (EIS). A platinum wires electrode was prepared as a counter electrode, an Ag/AgCl electrode as reference electrode, and the electrolyte was 6M KOH aqueous solution.

3. Results and discussion

The results of the X-ray diffraction were shown in Figure 3. An analysis of the scattering angle range of 10° to 80° revealed that peaks occurred at about 30° corresponding to the diffraction plane (002) of graphitic structure, compared with the JCPDS 75-1621 database, which according to Thazin *et al.* [4] and Paduuraksa group [15]. Water hyacinth activated carbon (WHac) is amorphous that less organized with gradual decreased in peak, possibly due to X-ray shots into the sample. in which the atoms are dispersed in an orderly manner.

The SEM image showed particle size at micro-scale within WHc and Whac (Figure 4). Figure 4(a) display that the surface roughness overlapped with a thick sheet (b). The WHac 600°C showed the surface roughness overlapped with the separated fracture within the same sheet and thickness. Figure 4(c) shows a surface with a uniform, smooth sheet, and thin plates. Finally, the WHac 800°C showed the surface slightly rough with disorganized and overlapping with the same sheet, but it's broken in some parts (as seen Figure 4(d)).

From Table 1, the surface area of the sample WHac 700 °C had the highest specific surface area and pore volume of 670.89 m^2 g^{-1} and showed the smallest pore size of 3.10 nm. The faster the electrolyte enters the surface area, the higher the charge. The comparison of the surface area and pore size of the total sample was shown in Table 1.

The isotherms of adsorption and desorption of nitrogen gas on WHc and WHac at 600, 700 and 800°C were found to be Type IV isotherms by the classification system of IUPAC (as seen in Figure 5), description of adsorbents with pores that are much larger than the diameter of the adsorbed molecules. Thus, the molecular arrangement at the surface of the adsorbent was bilayer. The properties of all samples were shown in Table 1. The WHc showed the largest pore size with the least specific surface area and activated carbon in a specific surface area between 76 $m^2 \cdot g^{-1}$ to 670 $m^2 \cdot g^{-1}$. The WHac 700°C sample has the smallest pore size and the highest specific surface area. According to previous work [19], the fabrication of carbon nanosheets from corncobs ramie fibers heat treatment at 700°C under an argon atmosphere shows a high surface area (718.81 $m^2 \cdot g^{-1}$) and high specific capacity (489 $mAh \cdot g^{-1}$ and 606 $mAh \cdot g^{-1}$) after 180 cycles.

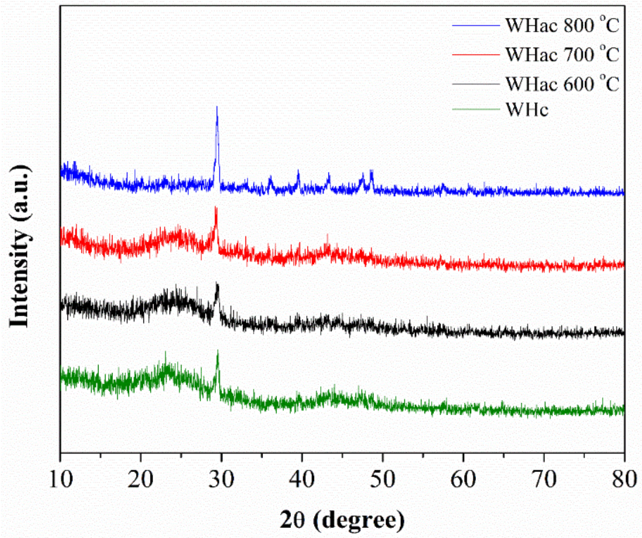

Figure 3. XRD pattern of WHc and WHac treated at 600°C, 700°C, and 800°C.

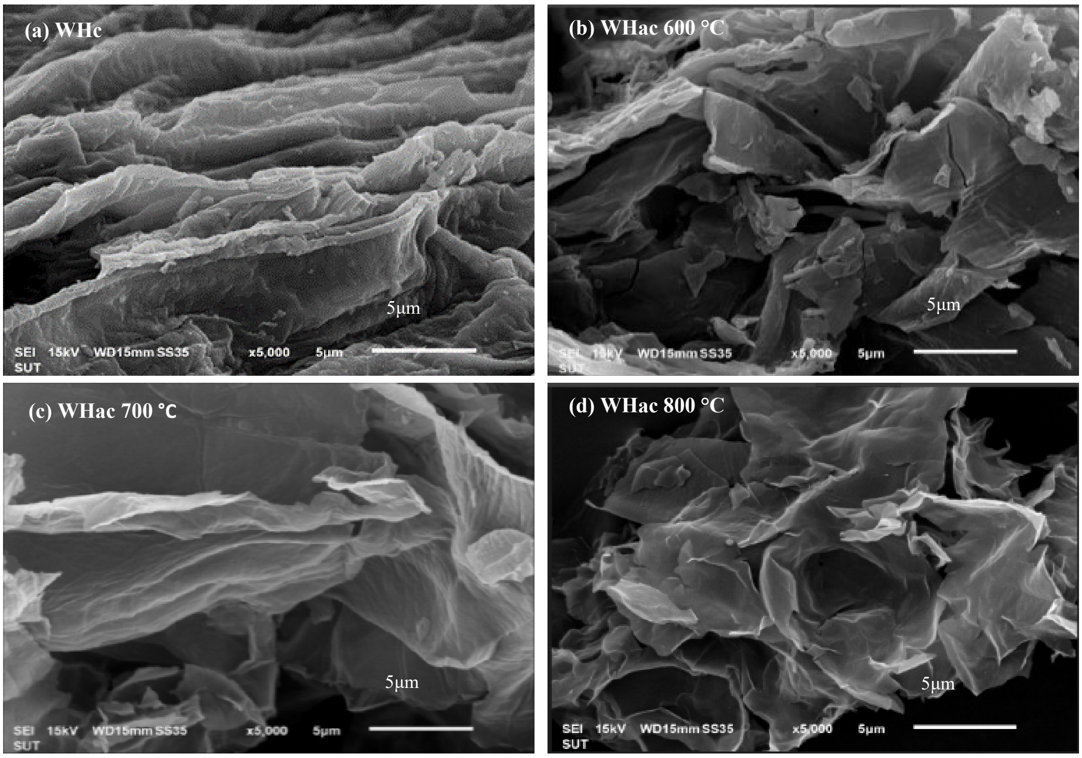

Figure 4. SEM pictures of (a) WHc, (b) WHac 600°C (c) WHac 700°C and (d) WHac 800°C.

Table 1 The specific surface area (S_{BET}), pore volume (V_{tot}), pore size (D_m), the resistance between electrodes and solution (R_s) and specific capacitance of WHc and WHac at temperatures of 600, 700 and 800°C.

Samples	**S_{BET} ($m^2 \cdot g^{-1}$)**	**V_{tot} ($cm^3 \cdot g^{-1}$)**	**D_m (nm)**	**R_s (Ω)**	**Specific capacitance ($F \cdot g^{-1}$)**
WHc	16.28	0.0400	9.8519	0.65	32.74
WHac 600 °C	76.38	0.0604	3.1625	0.91	46.77
WHac 700 °C	670.98	0.5208	3.1045	0.89	98.26
WHac 800 °C	547.08	0.4388	3.2087	0.87	17.62

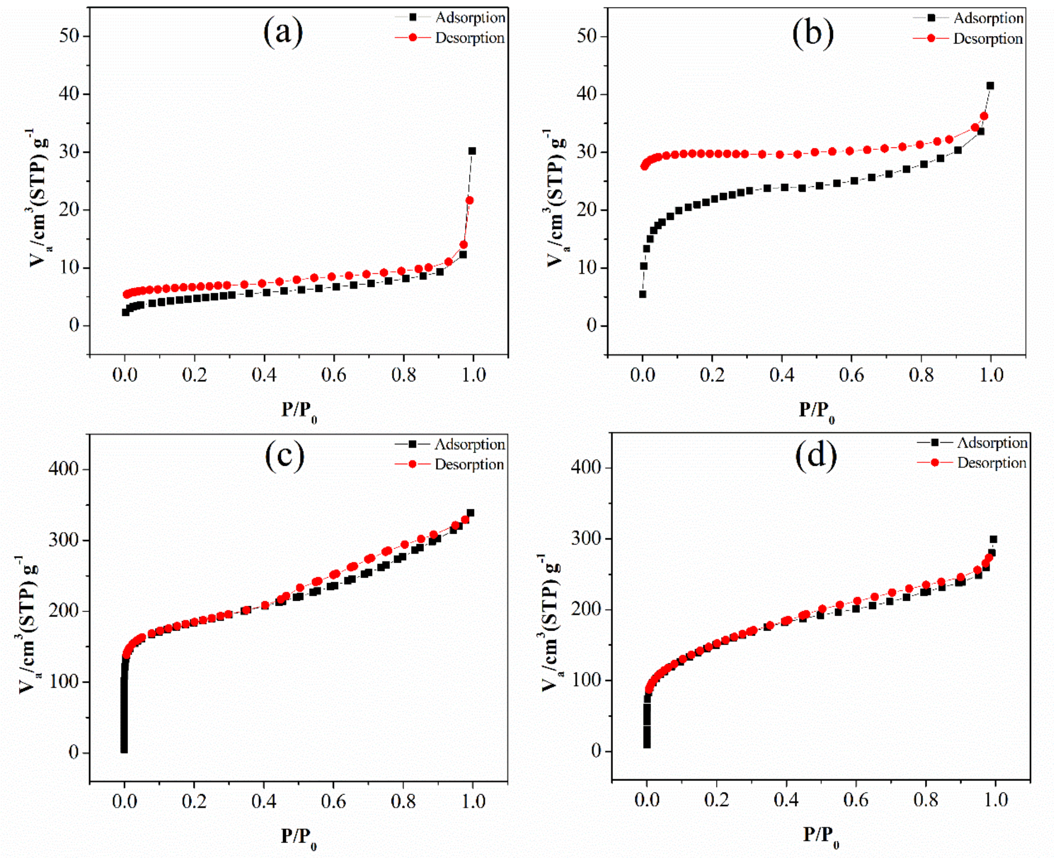

Figure. 5 The adsorption and desorption isotherms of (a) WHc, (b) WHac 600°C, (c) WHac 700°C, and (d) WHac 800°C.

Figure 6(a) shows the CV curves of all samples at a scan rate of 20 mV·s^{-1} with a potential rage of -1 V to -0.2 V. The results showed that the curves were rectangular, but not symmetrical, which indicates the electrochemical double-layer capacitor (EDLCs). The WHac 700°C sample had a greater area under the curve than the other sample, so the specific charge had the maximum value and the WHac 800°C sample had the area under the curve. Therefore, the specific capacitance was shown in Table 1. The specific capacitance can be calculated as in Equation (1) [8,16].

$$C_{CV} = \frac{1}{m v \Delta V} \int I dV \quad (1)$$

$$C_{CD} = \frac{I \Delta t}{m \Delta V} \quad (2)$$

where C_{CV} (F·g^{-1}) and C_{CD} (F·g^{-1}) are the specific capacitance from CV and GCD techniques, respectively. I is current (A), m is active mass (g) ΔV is potential windows (V), and Δt is discharge time (s).

Figure 6(b) shows the GCD curve that the relationship between charge and discharge times at a current density of 1 A·g^{-1}. It shows that the electrode exhibited of all samples are a triangle because of the electrochemical double-layer capacitor behavior of the sample. The sample with the highest discharging time were those with the longest discharging time and the best capacitance was WHac at 700°C, 600°C, WHc and WHac 800°C, respectively. The specific capacitance can be followed as in Equation (2) [8,16]. Capacitive the performant stability of all samples was measured as shown in Figure 6(c). The WHc was compared with WHac at different temperatures at a scan rate of 20 mV·s^{-1}, shows the life cycle stability of 96.74%, 98.69%, 98.26% and 99.57% of the WHc samples, WHac 600°C, 700°C, and 800°C, respectively. The present results indicated great electrochemical stability and were in good agreement with those reported in the literature [19,21]. The WHac 700°C decrease of only 1.74% the electrode operation in stable, with only a slight decrease, considered to show the best capacitance performance. The WHc sample was decreased with the least stable. At low frequency range WHac 700°C exhibits a more vertical curve than other samples, suggesting a better capacitive behavior. Figure 6(d) present that the EIS spectra of all samples. At high frequencies, the intercept of the Z' axis indicates the resistance between electrodes and solution (R_s). The R_s values of 0.65, 0.91, 0.89, and 0.87 Ω were observed for WHa, WHac 600°C, WHac 700°C, and WHac 800°C, respectively. A semicircle related to charge transfer resistance (Rct). The shortest diameter of the semicircle for the WHac 700°C indicates to lowest charge transfer resistance [17], while the largest diameter of the semicircle was observed in the WHac 800°C, leading to low electrochemical performance. A linear segment at low frequencies related to the Warburg resistance (W). This value is associated with the diffusion of electrolyte ions into the surface of the chemical electrodes. The vertical line represents the ion diffusion in the electrode and suggests a capacitive characteristic. It was found from the spectra that, the WHac 700°C exhibits a more vertical line, indicating nearly ideal capacitive behavior and low electrolyte ion diffusion resistance in the electrode material. Moreover, low values of R_s and R_{ct} and the smallest pore diameter, the largest surface area of WHac 700°C supported its excellent electrochemical performance [25].

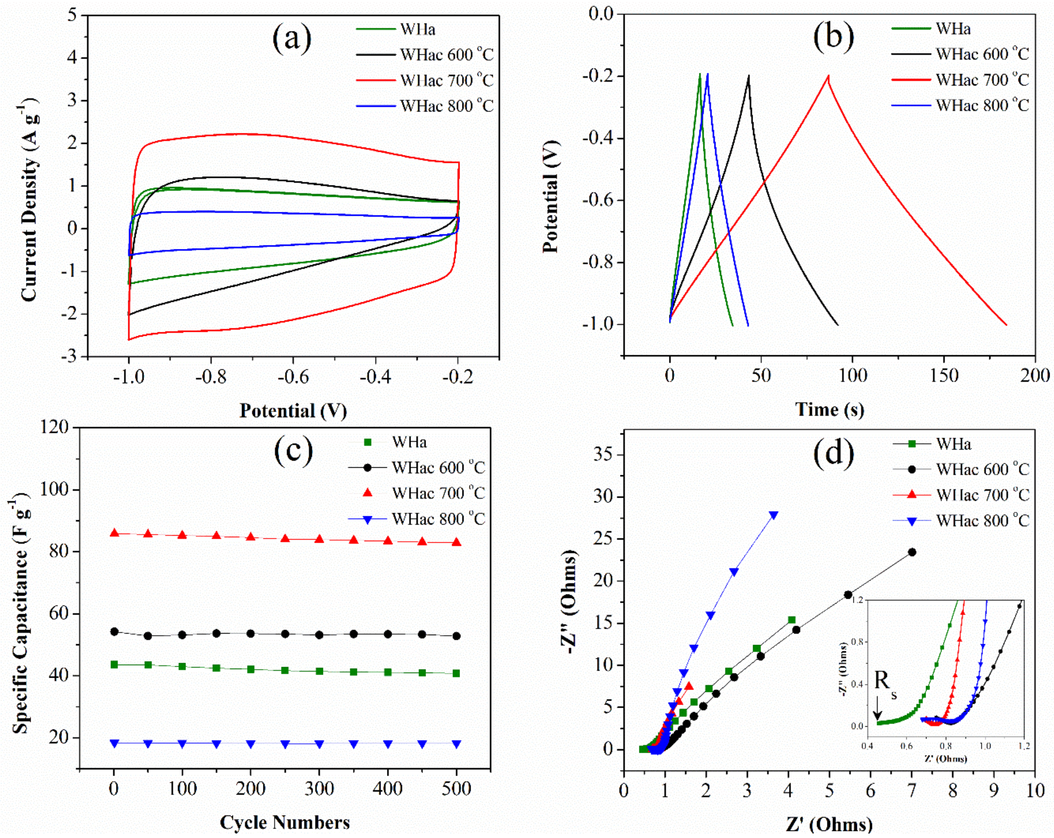

Figure 6. The electrochemical properties of all samples (a) the CV curve of all samples at scan rate of 20 mV·s^{-1}, (b) the GCD curve of all samples at a current density of 1 A·g^{-1}, (c) cycle stability of all samples at a current density of 1 A·g^{-1}, and (d) Nyquist plots.

4. Conclusions

In this research, the transformation of water hyacinth into activated carbon was performed from water hyacinth by thermal method. The uniform surface was not fractured, thin, not rough, and arranged in an orderly manner, being hold a charge better than rough, thick, uneven surfaces. The WHac 700°C showed a maximum charge of 98.25 F.g^{-1} with the slowest discharging and had 1.74% reduction in performance in the operation of the stable electrode, with only a slight decrease, considerably to be efficient in the performance of the capacitor as well. Based on compression and discharge measurements, water hyacinth activated carbon is suitable for energy storage devices as double layer capacitors (EDLCs) as an alternative energy device.

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