

## Preparation and characterization of micro porous activated carbon prepared from Prosopis Juliflora with chemical and thermal activation

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### Abstract

Activated carbon (AC) was developed from *Prosopis juliflora* wood by carbonization, chemical activation followed by thermal activation. The raw material was carbonized at 600 °C, then impregnated with potassium hydroxide (KOH) followed by thermal activation at 800 °C. Chemical and physical properties like moisture content, volatile matter, ash content, surface area and porosity have been estimated to determine the quality of AC as an adsorbent. The resulting sample was characterized by nitrogen adsorption measurement at 77 K, obtaining BET surface area 748.914 m<sup>2</sup>/g, micro pore volume 0.163 cm<sup>3</sup>/g and pore size 1.55 nm which indicate that the activated carbon synthesized was micro porous in nature. The surface functional groups were investigated by Fourier transform infrared spectroscopy techniques. Thermo gravimetric analysis was carried out to determine the thermal stability of activated carbon with respect to temperature. The surface morphology of activated carbon was performed by Scanning Electron Microscopy. X-ray powder diffraction was used for identification of crystalline nature of the prepared activated carbon. The prepared sample can be used to remove organic and inorganic pollutants from Industrial waste water.

**Keywords:** Activated carbon, Carbonization, *Prosopis juliflora*, Potassium hydroxide, Chemical activation, Thermal activation.

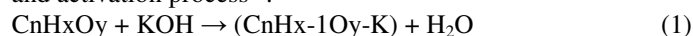
### Introduction

Activated carbon (AC) is a solid material, black in colour and highly porous in nature, and a well established adsorbent due to micro porosity, higher surface area and large pore volume and greater extent of surface reactivity<sup>1</sup>. Depending on its physical nature, it is available in various forms such as granular form, powdered form, fibrous form and pellet form<sup>2</sup>. Activated carbon can also be divided on the basis of size of pores: macro pore (pore size greater than 50 nm), meso pore (50 nm > Pore size > 2 nm) and micro pore (pore size less than 2 nm). AC has been employed for the treatment of Industrial waste water, to remove harmful components like heavy metals<sup>3,4</sup>, dyes<sup>5,6</sup> pharmaceutical residues<sup>7,8</sup> and purification of drinking water<sup>9</sup>. AC can be used not only for gas phase adsorption but also for liquid phase adsorption<sup>10</sup>. However, the liquid-phase application of AC is more significant compared to gas phase applications<sup>11</sup>.

AC can be synthesized by either a physical activation or Chemical activation method<sup>12</sup>. Chemical activation is a one step process in which the raw precursor is impregnated with a chemical, an activating agent, followed by carbonization. Commonly used chemicals, as activating agents, are Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), Nitric acid (HNO<sub>3</sub>), Potassium hydroxide (KOH), Zinc chloride (ZnCl<sub>2</sub>) and Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>). Physical activation is a two stage process in which carbonization takes place first followed by activation. AC is generally prepared from a carbonaceous material like

wood, coal, lignite and agro residues like tamarind wood<sup>12</sup>, sugarcane bagasse<sup>13</sup>, rice husk<sup>3</sup>, coconut shell<sup>1</sup>, palm shell<sup>14</sup>, pomegranate shell<sup>15</sup>, banana peel<sup>16</sup> and coir pith<sup>17</sup>.

*Prosopis juliflora* chosen for preparing AC in this present study is a type of weed<sup>18</sup>. This thorny shrub has a serious impact on ground water as it depletes the level of water since it has a tendency to absorb groundwater and in its absence, it consumes water by absorbing it from atmospheric moisture. No other plant species can co-exist with *Prosopis Juliflora*<sup>19</sup>. It is a great threat to water bodies such as lake, river and irrigation systems<sup>20</sup>. In this research, *Prosopis juliflora* wood has been selected as raw precursor for the preparation of AC. The carbonization of *Prosopis juliflora* wood was carried out at 600°C followed by impregnation with KOH. After impregnation, the sample was subjected to thermal activation at 800°C. The reactions given below take place during KOH impregnation with raw precursor and activation process<sup>21</sup>:

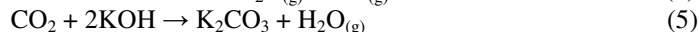
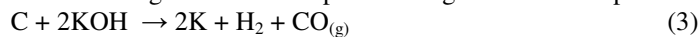


The semi carbonization is the first step and it can be shown as:  
(C<sub>n</sub>H<sub>x</sub>-1O<sub>y</sub>-K) → Char (+K) + Tars + Gases (2)

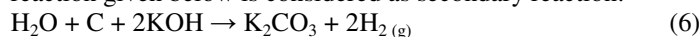
Char usually includes < 80% carbon; Oxygen (15-20%) and less percentage of Hydrogen.

Phenols, Acetic acid, Methanol, (CH<sub>3</sub>)<sub>2</sub>CO, and other hydrocarbons are the components of tar. The major gaseous components are H<sub>2</sub>O, CO<sub>2</sub>, CO.

The following reactions take place during the activation process:



During activation, Potassium gets introduced with the carbon matrix, tending to the formation and enhancement of pores. The reaction given below is considered as secondary reaction:



The objective of the present study is to prepare micro porous AC from Prosopis juliflora wood and to subsequently use it for the treatment of Industrial wastewater. The synthesized AC was characterized by Ultimate analysis, proximate analysis, Scanning electron microscopy (SEM), Fourier transform IR spectroscopy (FTIR), X ray diffraction (XRD) and BET surface area analyzer.

## Materials and methods

**Preparation of Activated Carbon (AC):** The preparation of AC in the present investigation is a two stage process: i. carbonization and ii. activation. The carbonization is basically to enhance the carbon content and initialization of pores while the second step helps in developing the pore structure<sup>12</sup>. The Prosopis juliflora wood was collected from NIT Tiruchirappalli campus and the wood was cut into 5-10 mm size pieces. The method of preparation of activated carbon is as follows:

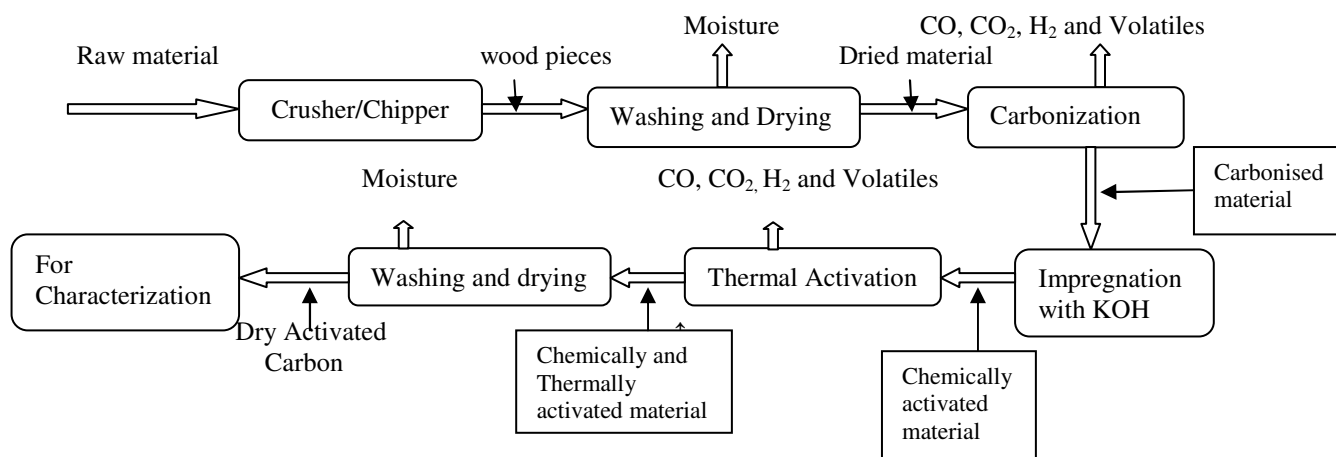
The Prosopis juliflora wood was cleaned using distilled water to remove dust and dirt particles. Wood pieces were then sun dried and carbonized in the tubular furnace at 600°C for 1 hr in the presence of N<sub>2</sub> gas with flow rate of 100 cm<sup>3</sup>/min. The carbonized sample was then crushed and separated into 125-150 micrometer size. The charcoal was then impregnated with Potassium Hydroxide (KOH) for 8 hours. The Chemical ratio

(activating agent/raw precursor) was kept 1:1 and then the wet activated carbon was kept in the Vacuum drier for 2 h. at 75°C then the dried sample was kept in Tubular furnace at activation temperature of 800°C for 1 h. in nitrogen atmosphere to increase the porosity of the AC. The activated carbon was further washed by HCl (0.1M) and NaOH (0.1M) and distilled water to remove residuals. The resulting AC was dried in the hot air oven at 110 °C for 2h, and then kept in the dry container. The various stages involved in the preparation of AC from a woody material are given in Figure-1 as a schematic diagram.

### Characterization of Activated Carbon: Physical

**Characterization:** The important characteristics of AC such as specific surface area, pore volume and pore size of the synthesized AC were measured using Micromeritics TriStar 3000 V6.07 A. Bulk density was calculated by water displacement method<sup>22</sup>. Bulk density of AC was noted to be 0.704 gm/cc. Surface morphology of AC was studied using Scanning Electron Microscopy. SEM image was obtained using F E I Quanta FEG 200 - High Resolution SEM instrument. The Quanta 200 FEG also detects the presence of elements or any solid conducting materials through the EDX.

**Chemical Characterization:** Moisture content, volatile matter, fixed carbon and ash content for both precursor and AC were estimated by proximate analysis. The ultimate analysis determines the elements present in the sample, both in precursor and AC, such as carbon, hydrogen, oxygen, nitrogen, and sulphur. The elemental analysis of the sample was conducted using elemental make vario micro cube model CHNS analyzer. The amorphous nature of AC was confirmed by X-ray diffractometer. The FT-IR spectrum was recorded using a Perkin Elmer 4000 spectrophotometer to analyze the surface functional groups present in the AC. The FTIR spectrum was registered from 4000 to 400 cm<sup>-1</sup>.



**Figure-1:** Schematic diagram for steps involved in the Preparation of AC from Prosopis juliflora

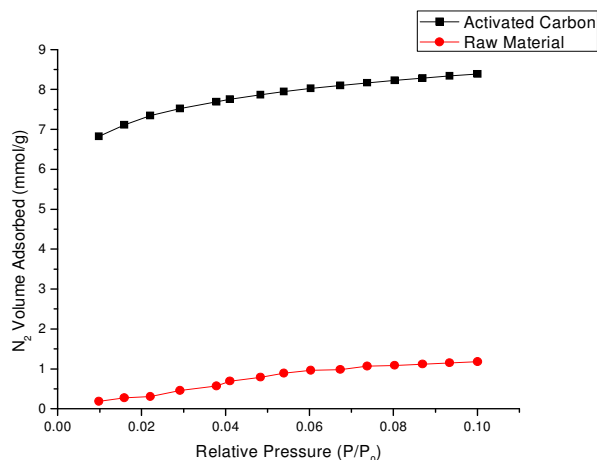
## Results and discussion

**BET Surface Area Analysis:** In Table-1, the BET surface area, total pore volume, micro pore volume and pore size for both precursor and activated carbon are shown. The surface area of the raw precursor and AC were measured in the relative pressure range of 0.009 to 0.1 using BET method. The N<sub>2</sub> adsorption isotherms at 77 K of both raw material and AC are shown in Figure-2. Before N<sub>2</sub> gas adsorption measurements, the sample was degassed at 90°C for 1h and at 300°C for 16 h in presence of vacuum. The pore size of the activated carbon is 1.55 nm which indicates AC possess a microporous structure while the pore size of raw precursor is 2.704 nm which means mesopores are available in raw precursor.

The activated carbon shows higher surface area than raw precursor because of presence of micropores in the AC that formed during carbonization and activation stages. The BET surface areas of raw material and AC are 68.671 m<sup>2</sup>/g and 748.914 m<sup>2</sup>/g respectively.

**Table-1:** BET Analysis Results.

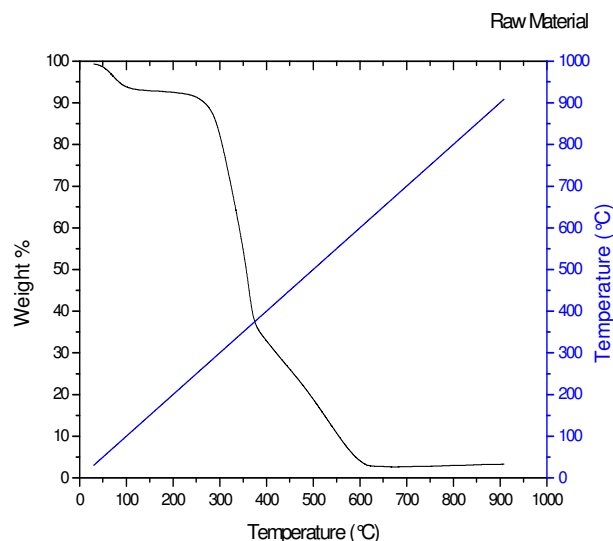
Properties	BET Surface Area (m <sup>2</sup> /g)	Total Volume (cm <sup>3</sup> /g)	Micro pore Volume (cm <sup>3</sup> /g)	Pore Size (nm)
Raw Precursor	68.671	0.0464	0.0118	2.704
Activated Carbon (AC)	748.914	0.291	0.163	1.553



**Figure-2:** N<sub>2</sub> Adsorption isotherms.

**Thermogravimetric Analysis (TGA):** The TGA curve of the raw precursor is shown in Figure-3 and the studies were conducted in N<sub>2</sub> atmosphere in the temperature range of 30 to

900°C. Heating rate of 10°C/min was kept constant throughout the experiment for this study to see the weight loss behaviour of the sample on heating. The reduction in weight in the temperature range 30°C to 280°C is represented by the first step and this weight loss corresponds to the removal of moisture and surface bounded water. In the temperature range from 280°C to 370°C, a rapid weight loss is seen. This phenomenon of weight loss is due to the decomposition of cellulose as well as furan derivatives. Beyond temperature of 370°C, a gradual weight loss is observed and this continues till it reaches a temperature of 650°C. This weight loss is observed due to decomposition of hemicellulose and lignin. Hence, the range of 400°C to 650°C is chosen for carbonization in the present study.



**Figure-3:** TGA curve for raw precursor.

**Proximate and Ultimate Analysis:** The results of proximate analysis and ultimate analysis for both precursor and activated carbon are shown in Table-2 and 3 respectively. The results show that the fixed carbon content in AC is high as compared to raw precursor which makes it a suitable material for adsorption applications. Ash content is the left over matter when the carbonaceous part is burned off. Ash is an impurity present in the AC and it includes mainly minerals like aluminum, silica, iron, calcium etc.

The ash content of AC is 0.92% as shown in Table-3, which favors the quality to be a good adsorbent. From the ultimate analysis it has been observed that oxygen, Hydrogen, Nitrogen and Sulphur content decreased in the activated carbon because of the decomposition of raw material during carbonization and activation. During this decomposition, the volatiles which contain H, N and O escape from the carbonaceous part, making wood rich in carbon content. From Table-3, it is observed that, carbon content increased from 45.20 wt % to 79.81wt % and at the same time oxygen and hydrogen content decreased from 51.50 wt % to 17.04 wt% and 5.58% to 2.48% respectively.

**Table-2:** Proximate Analysis for Raw precursor and AC.

Sample	Moisture (wt.%)	Volatile matter (wt. %)	Fixed Carbon (wt %)	Ash (wt.%)
Raw Precursor	10.85	72.83	14.47	1.85
Activated Carbon (AC)	2.98	17.54	78.56	0.92

functional group is confirmed by the peak at 3000  $\text{cm}^{-1}$ , which is not observed in AC. This suggests that the notable amount of hydrogen was removed during activation step itself. The reduction of Hydrogen is well supported by ultimate analysis results shown in Table-3, which indicates a decrease in hydrogen content up to 55.55 % in AC. The peak at 1740  $\text{cm}^{-1}$  observed for precursor shows the presence of C=O functional group and it is not available in the AC, which indicated that many bonds have been cracked during chemical activation process and eliminated light components along with volatiles<sup>10</sup>. The band at 1575  $\text{cm}^{-1}$  in AC is associated with C=C functional group. The functional group C-H symmetric bending and asymmetric bending for AC is confirmed by peaks at 1375  $\text{cm}^{-1}$  and 1450  $\text{cm}^{-1}$  respectively. The band at 1000  $\text{cm}^{-1}$  is seen in both AC and raw precursor, indicating the presence of C-O functional group.

**Fourier Transform IR Spectroscopy (FTIR):** The FT-IR analysis was conducted for AC and raw precursor. FT-IR spectra of the raw precursor and AC are shown in Figures-4 and 5 respectively. The presence of asymmetric C-H stretching

**Table-3:** Ultimate Analysis for Raw precursor and AC.

Sample	C (wt.%)	H(wt.%)	N(wt.%)	S (wt.%)	O(wt.%)
Raw Precursor	45.20	5.58	0.65	0.07	51.50
Activated Carbon (AC)	79.81	2.48	0.61	0.06	17.04

**Table-4:** FT-IR Analysis.

Raw precursor	Wave number, $\text{cm}^{-1}$	750	1000 and 1250	1740	1800	3000	
	Assignments	phenyl group	Carboxylic group in carboxylic acids, esters, alcohol and phenols	C=O Stretching in esters	C=O in amides, ketones, aldehydes and carboxylic acid	=C-H alkene or arene	
Activated carbon	Wave number, $\text{cm}^{-1}$	600 and 700	750	1000 and 1200	1375	1450	1575
	Assignments	C-C Stretching	phenyl group	Carboxylic group in carboxylic acids, phenols, esters and alcohols	C-H Asymmetric and symmetric bending	C-H Asymmetric bending	C=C Stretching band

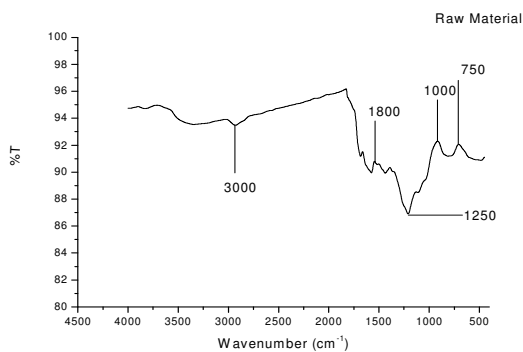


Figure-4: FTIR spectra of raw precursor.

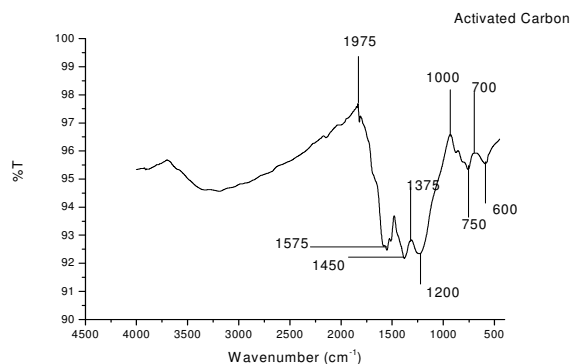


Figure-5: FTIR spectra of Activated Carbon.

**Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectrometry (EDX) Analysis:** Figure-6 shows SEM image of AC and it indicates clearly a highly micro porous surface with honeycomb shaped micro pores. The volatiles which are removed during the carbonization and activation process generate a highly fixed carbon network with porous structure. The elemental analysis of AC was done by using EDX analysis and is shown in Figure-7. In Table-5, the results in terms of weight percentage and atomic percentage are given. From the Table-5, it is observed that carbon is the major component present in AC.

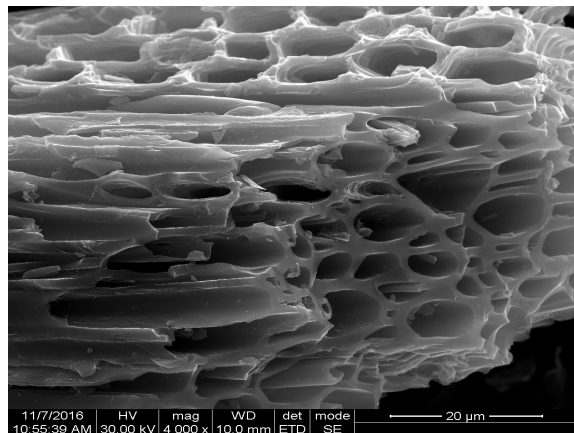


Figure-6: SEM image of Activated Carbon.

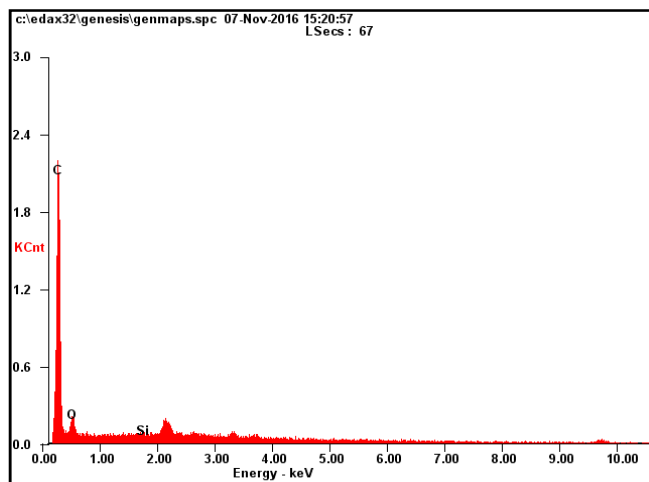


Figure-7: Image of EDX analysis.

Table-5: EDX analysis of Activated Carbon.

Element	Wt%	At%
C K	85.06	88.40
O K	14.80	11.54
Si K	00.14	00.06

**X-Ray Diffraction (XRD) Analysis:** XRD analysis was carried out for the identification of crystalline nature of activated carbon and raw precursor and is shown in Figures-8 and 9 for precursor and AC respectively. From the Figures-8 and 9, it has been observed that activated carbon has an amorphous structure and the absence of sharp peak indicates non-crystalline phase. Raw precursor shows same profile as that of AC except a peak at 32°.

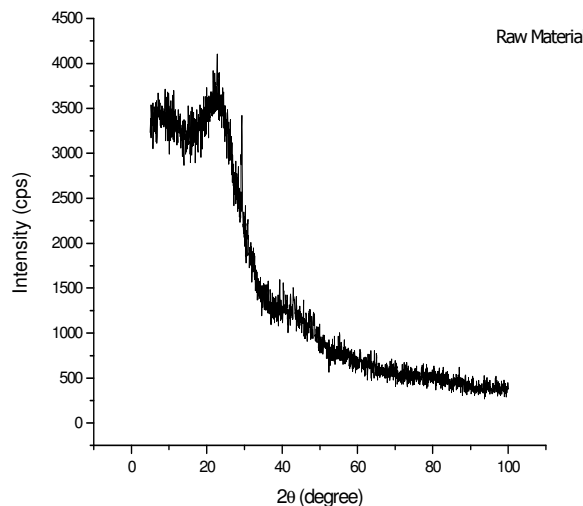


Figure-8: XRD profile for Raw Precursor.

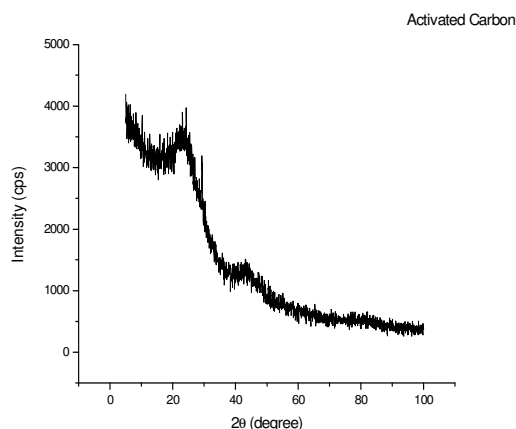


Figure-9: XRD profile for Activated Carbon.

## Conclusion

The micro-porous AC from *Prosopis juliflora* wood was successfully prepared by chemical and thermal activation and characterized. The AC synthesized showed very high surface area, high pore volume and micro porosity as compared to raw precursor. SEM analysis confirmed a highly porous structure for AC and EDX analysis proved that major component present in the AC is carbon. Thermal stability of raw precursor is found to be good by TGA analysis. From the above results, it is believed that the AC synthesized can be used effectively to remove organic and inorganic pollutants from industrial wastewater.

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