



## Preparation and characterization of chemically activated carbons from different varieties of date stones

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### ABSTRACT

Three activated carbon, Ghers Biskra (ACGB), Mech Biskra (ACMB) and Ghers El-Oued (ACGE) were prepared and characterized from date stone of the south of Algeria. The activation was achieved chemically by using phosphoric acid as an agent. The resulting materials were characterized by different techniques such scanning electron microscopy and Fourier transform infrared (FTIR) spectroscopy. The textural characterization was based on the evaluating of two major parameters: surface area and micropore volumes. The Brunauer–Emmett–Teller (BET) surface area and micropore volumes of optimized activated carbon ACGB, ACMB and ACGE were found to be 1,118, 950 and 749 m<sup>2</sup>/g and 0.52, 0.46 and 0.37 cm<sup>3</sup>/g, respectively. The analysis and the comparison of the experimental data show that the best parameters have been obtained with the ACGB date stones coming from Biskra region; a micro porosity of 93.64% and a pore radius of 8.95 Å were measured. Size microspores and energy of activation were determined by Dubinin–Radushkevich isotherm model. The functional groups of the different activated carbon surfaces were characterized by Boehm method and FTIR spectroscopy.

*Keywords:* Date stones; Activated carbon; Chemical activation; Adsorption; Isotherm; Porous texture

### 1. Introduction

Over the last 2 decades, the pattern of industrialization has been tremendously changed leading to a remarkable imbalance of the ecosystem. Consequently, the contamination of potable underground and surface water reservoirs have become the worldwide phenomenon. Preserving this vital resource is a major challenge that must be addressed in the coming years. The contemporary environmental researcher is looking for potential material to separate the contaminant from the potable water. Highly porous activated

carbons activated carbons have been the “working horse” of many research works. Lignocelluloses resources such as cherry stones [1–4], waste tea [5–7], apricot stones [8], olive stones [9,10], oil-palm stones [11], walnut shells [12], cattail [13], coconut shells [14–16], tobacco residues [17], rice husks [18], walnut and poplar woods [19], cotton stalk [20–22], fruit juice industry [23,24], acacia mangium wood [25] and date stone [26–32] are well-known precursors in the production of such materials.

Date stones are abundant by-products of date palm industry in the south of Algeria. In an attempt to valorize this well known material, we have chosen three varieties

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of date stones coming from two different regions: Biskra and El-Oued. The selected varieties are called Ghers Biskra (ACGB), Mech Biskra (ACMB) and Ghers El-Oued (ACGE).

The principal aim of this study is the preparation of activated carbons using phosphoric acid as dehydrating agent for the chemical activation of these three deferent local date stones. The performances of the prepared activated carbons (expressed in terms of micropore volumes and specific surface area) are studied. The characterization is performed, using Boehm titration and Fourier transforms infrared (FTIR) spectroscopy for the chemical structure and scanning electron microscopy (SEM) for the morphology. Finally, the textural characterization of ACGB, ACMB and ACGE is discussed.

## 2. Materials and methods

### 2.1. Preparation of the activated carbon

The effect of change in activation time and temperature was optimized. A series of experiments have been conducted to study the effects of different carbonization temperatures (400°C, 600°C, 800°C and 1,000°C) with different activation times (90, 120, 150, 180 and 210 min) at activation temperature of 600°C. Thus, the different activated carbons of ACGB, ACMB and ACGE were prepared as follows: date stones were firstly washed many times with distilled water until getting rid of impurities. The obtained solid was dried in a micro oven at 105°C overnight and then served; the selected fraction has an equivalent diameter less than 0.5 mm.

Chemical activation of the precursor was conducted with  $H_3PO_4$ . Thirty four grams of dried precursor were well mixed with 40 mL of phosphoric acid aqueous solution of volumetric ratio (1/1). The mixture was being stirred at 100°C during 1 h. Pyrolysis of the resulting granular particles was performed at 600°C during 3 h. The activated carbons was washed abundantly by 10% HCl to eliminate carbonization residues and with distilled water until neutralization (the pH value was 7.35, 6.98 and 6.86 for ACGB, ACMB and ACGE, respectively). Finally, the prepared activated carbons were dried at 105°C during at least 8 h and stored in closed bottles.

### 2.2. Characterization of the activated carbons

Characterization was based on the determination of the following parameters: bulk density, surface functional groups and porosity. All these experimental details were presented in reference [33]. The elemental analysis was performed by the spectroscopy X-rays with photoemission (XPS).

#### 2.2.1. Surface functional groups

The surface acidic oxygen containing functional groups were determined by Boehm titration [35], one of the most widely used methods to quantify acidic groups on the surface of activated carbons. The Boehm titration assumes that strong base such as sodium hydroxide (NaOH) (0.05 mM) neutralizes carboxylic, lactonic and phenolic groups; sodium carbonate ( $Na_2CO_3$ ) neutralizes carboxylic and lactonic groups; and weak base sodium bicarbonate ( $NaHCO_3$ ) at the same concentration (0.05 mM) only neutralizes strong acidic groups such as carboxylic groups. In this work, 1 g of the

sample was mixed with 25 mL of 0.05 mM each base solution in a 50-mL beaker covered with parafilm. After stirring at room temperature for 24 h, followed by filtration with Whatman filter paper, 10 mL of the filtrate was titrated with 0.05 mM hydrochloric acid (HCl) using a Mettler Toledo Autotitrator (T70, Mettler Toledo, Columbus, OH, USA). The number of acidic sites was determined with the assumption that the three types of base solutions used can completely neutralize the acidic groups on the activated carbon surface.

#### 2.2.2. Porosity

Pore structure of the different prepared activated carbons was evaluated by measuring nitrogen adsorption-desorption isotherm at 77 K using an automatic instrument (Quantachrome Instruments, Model NOVWIN2). The cross-sectional area of nitrogen molecule was taken equal to 0.162 nm<sup>2</sup> [33]. The specific surface area ( $S_{BET}$ ) was evaluated by the Brunauer–Emmett–Teller (BET) equation [35] when the relative pressure in the range of 0.05–0.30. Micropore area and micropore volume were determined by the *t*-plot method whereas the total pore volume was directly calculated from the volume of nitrogen held at the highest relative pressure ( $P/P^0 = 0.9878, 0.9886$  and  $0.9860$ ) for ACGB, ACGE and ACMB, respectively. The total pore volume,  $V_T$ , is often determined from the amount of vapor adsorbed at a relative pressure close to unity by assuming that the pores are filled with condensed adsorptive in the normal liquid state [36]. The total mesopore volume was calculated from the difference between total and micropore volumes. External surface area ( $S_{ext}$ ) is that associated to the non-microporous structure (macroporous and mesoporous) [37]. The mesopore area was calculated by subtracting the micropore area from the BET surface area; the pore volume and size distribution were determined from the density functional theory (DFT) [37,38].

The range of porosity was described according to the international union of pure and applied chemistry (IUPAC) by distinct areas: ultra micropores (the diameter pore size,  $D < 0.7$  nm) and the super micropores ( $0.7 < D < 2$  nm), the mesopores ( $2 < D < 50$  nm) and macropore ( $D > 50$  nm) [39,40].

The values of  $S_{micro}/S_{BET}$  indicate the predominance of micropore volumes, and they are consistent with the calculated values of  $V_{micro}/V_T$  [28].

The isotherm model of Dubinin–Radushkevich (D–R) applied from the adsorption isotherms of  $N_2$  to 77.33 K for the different activated carbons to determinate the micropore volume ( $V_{DR}$ ), the pore size ( $L$ ) and characteristic adsorption energy ( $E_0$ ). The D–R method developed the micropore volume filling theory [40].

#### 2.2.3. Morphological analysis

SEM technique has been used to obtain information on the morphology and size of the samples. The morphology was studied using Quanta 600W environmental scanning electron microscope (ESEM) operated at accelerating voltages of 2 kV with magnification of 15,000X. The particles were glued to a metallic sample holder using a carbon double-sided tape and then coated with platinum to prevent the charging effect.

### 2.2.4. Determination of pH and $pH_{pzc}$

The pH of activated carbons of ACGB, ACMB and ACEG was determined according to ASTM D6851 method by mixing activated with deionized water at ratio of 1:10 and the pH measured by a pH meter (WTW inoLab model). The pH measurements were carried out in triplicates at room temperature. Point of zero charge (pzc) of biochars ( $pH_{pzc}$ ) was measured by placing 100 mL of 0.01 mol/L NaCl solution in a closed polyethylene bottle. The pH was adjusted between 2 and 12 by adding HCl or NaOH 0.1 mol/L solution. Then, 0.05 g of each sample was added in the closed polyethylene bottle that was set stirring for 5 d at the room temperature before measuring the final pH. Then the final pH was plotted against the initial pH, and the point where this curve crosses the line  $pH_{final} = pH_{initial}$  represents the  $pH_{pzc}$ .

### 2.2.5. FTIR spectroscopic analysis

The surface functional groups and structure of the resulting activated carbons were studied by FTIR spectroscopy recorded between 400 and 4,000  $cm^{-1}$  in a spectrometer Shimadzu using the KBr wafer technique.

## 3. Results and discussion

### 3.1. Effect of parameters of activation

The effect of change in activation time and temperature, which most significantly influence the physicochemical characteristics including surface area, bulk density and yield of the adsorbent, was optimized. The results showed that 600°C temperature for 180 min carbonized date stones char had higher BET surface area, total volume, micropore volume and yield as compared with other conditions. The optimal pyrolysis temperature is then fixed at 600°C for 3 h of activation. Thus, all the samples are pyrolyzed at this temperature and time; similar results were reported by Danish et al. [31].

### 3.2. Textural properties of the activated carbons

The adsorption isotherm represented in Fig. 1 provides qualitative information on the adsorption process. All isotherms of the activated carbons series present a dense micropore structures (dimensions < 20 Å) [41], which belong to type I according to IUPAC classification [36]. The presence of small hysteresis ( $H_4$ ) shape in the desorption curve indicated the presence of mesoporosity associated with small contribution of mesopore and possible occurrence of a capillary condensation phenomenon. In addition, it was suggested that the carbon products contained mostly micropores. Details of texture properties of the carbon materials produced are summarized in Table 1. The surface area and pore volume of activated carbon prepared of the optimum variety were 1,118  $m^2/g$  and 0.52  $cm^3/g$ , respectively. The pore size distribution of the material is shown in Fig. 2; as it can be seen, the majority of pores have diameter smaller than 20 Å, which corresponds to 93.64% of the microporosity, with 6.36% of mesoporous. Additionally, the mean pore radius value was 8.95 Å. The best value of surface area  $S_{BET}$  of activated carbon obtained comparable

with other surface area realized by relating other techniques and using different or similar precursors of activated carbon. For example, the activated carbons from date stones reported by Ahmed and Theydan [27] using zinc chloride and ferric chloride as activating reagent found  $S_{BET}$  of 780.06 and 1,045.61  $m^2/g$ , respectively. The activated carbon of date stones prepared by physical activation with carbon dioxide reported by Sekirifa et al. [28] showed  $S_{BET}$  of 604  $m^2/g$ . Chaouch et al. [42] and M.Z.S. Hazourli and A. Hazourli [43] prepared an activated carbon by phosphoric acid when

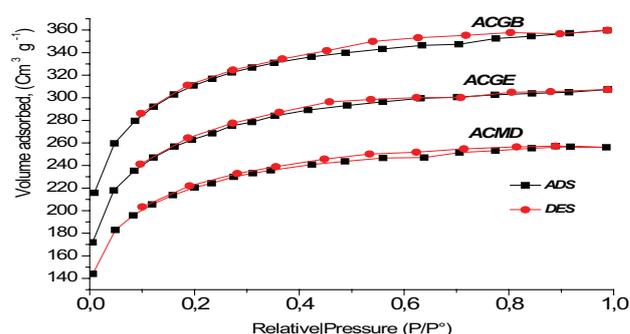


Fig. 1. Nitrogen adsorption isotherms for the three varieties of activated carbon.

Table 1

Textural and chemical properties for the three varieties of activated carbon: ACGB, ACEG and ACMB

Properties	Methods	ACGB	ACEG	ACMB
$S_{BET}$ ( $m^2/g$ )	BET	1,118	950	794
$V_T$ ( $cm^3/g$ )	Single point adsorption	0.56	0.48	0.40
$V_p$ ( $cm^3/g$ )	DFT	0.50	0.43	0.36
$S_{ext}$ ( $m^2/g$ )	<i>t</i> -plot	21	13	26
$S_{micro}$ ( $m^2/g$ )		1,097	937	767
$V_{micro}$ ( $cm^3/g$ )		0.52	0.46	0.37
$V_{meso}$	$VT - V_{micro}$	0.04	0.02	0.03
$r_p$ (nm)	$2V_p/S_{BET}$	0.89	0.9	0.91
$S_{micro}/S_{BET}$ (%)		98	99	97
$S_{ext}/S_{BET}$ (%)		2	1	3
$V_{micro}/V_T$ (%)		93	96	92
$V_{meso}/V_T$ (%)		7	4	8
$V_{micro}$ ( $cm^3/g$ )	D-R plot	0.43	0.37	0.31
$L$ (nm)		1.85	1.85	1.85
$E_0$ (kJ/mol)		4.28	4.28	4.28
Functional groups				
$V_{carboxylic}$ (meq/g)	Boehm titration	1.40	1.90	2.55
$V_{lactone}$ (meq/g)		0.30	0.60	0.05
$V_{phenolic}$ (meq/g)		0.45	0.13	0.20
$V_{acidic}$ (meq/g)		2.15	2.63	2.80
$V_{basic}$ (meq/g)		0.50	1.00	0.25

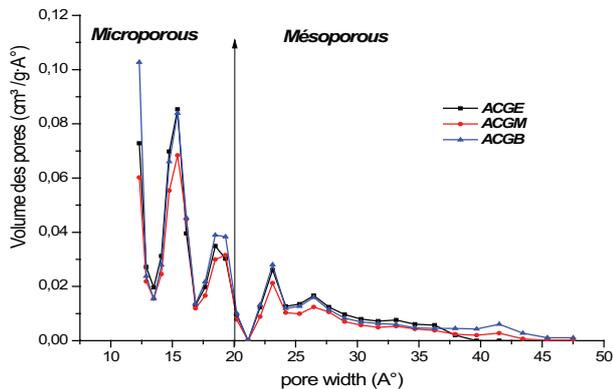


Fig. 2. DFT pore size distribution for the three varieties of activated carbon.

found the surface area 54.934 and 1,100  $\text{m}^2/\text{g}$ , respectively. The carbon percentage of ACGB, ACMB and ACGE samples as determined by elemental analysis (wt%) are found as follows: 89.83, 85.86 and 87.94, respectively. It seems from the results of these samples that the C % is directly proportional to the surface area, i.e., to the high porosity of the activated carbon.

D–R plots of the nitrogen adsorption isotherms of all activated carbon (ACGB, ACGE and ACMB) showed in Fig. 3. The textural parameters of the equilibrium model of D–R isotherm were summarized in Table 2. The value of the micropore size ( $L$ ) is of order 1.85 nm, and the activation energy was 4.28 kJ/mol, which corresponds to a physisorption.

The significance of  $\text{pH}_{\text{pzc}}$  of a given activated carbon surface is that when the pH is lower than the pzc value, the activated carbon surface is positively charged (attracting anions). Conversely, above pzc, the surface is negatively charged (attracting cations/repelling anions). The  $\text{pH}_{\text{pzc}}$  of activated carbons of ACGB, ACMB and ACGE were found to be 4.31, 4.02 and 6.14, respectively. The pH values of the activated carbons ranged from 6.68 to 7.35. Thus, the  $\text{pH}_{\text{pzc}}$  of the activated carbons was less than the pH of the activated carbon indicating richness in negative charges on the activated carbon surface. It follows that ACGB, ACMB and ACGE are suitable for cationic pollutants removal in slightly basic solution.

The results of elemental analysis of the ACGB, ACMB and ACGE studied in XPS permit to determine the chemical composition of surface, expressed in atomic percentages. It can be seen from Table 2 that the essential of the carbonized or activated matter is the carbon. The high percentage of this element (>80%) represents well a traditional structure of carbon. This interprets a good chemical activation and pyrolysis of the date stones.

### 3.3. FTIR spectra and SEM micrographs

The FTIR spectra provide valuable information about the chemical compositions of the activated carbons (Fig. 4). The spectra have the following absorptions bands for ACGB, ACGE and ACMB, respectively: The bands observed at 3,420–3,426  $\text{cm}^{-1}$  are indicative of the  $\nu_{\text{OH}}$  stretching vibration and existence of alcohol, phenol and carbonyl groups. The bands at 1,554, 1,548 and 1,561  $\text{cm}^{-1}$  could be attributed to

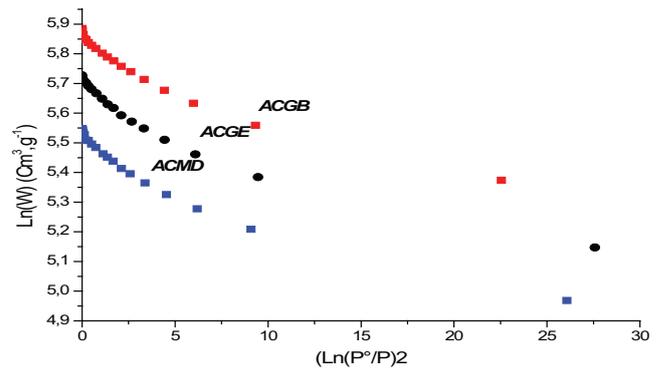


Fig. 3. D–R plots of the nitrogen adsorption isotherms of all activated carbon ACGB, ACGE and ACMB.

Table 2

The elemental analysis of the three date stones: ACGB, ACMB and ACGE

Date stone	% C	% O	% N	% P
ACGB	86.33	8.51	1.81	2.24
ACMB	84.80	12.40	1.43	1.48
ACGE	84.18	13.02	0.19	2.21

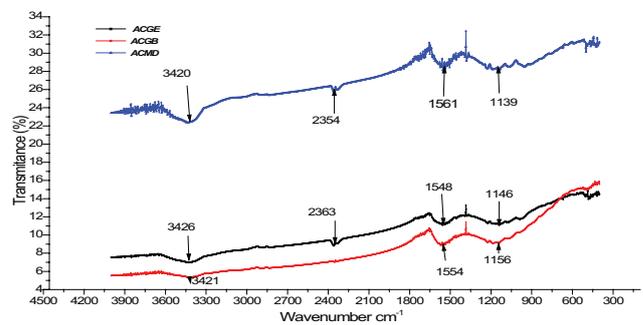
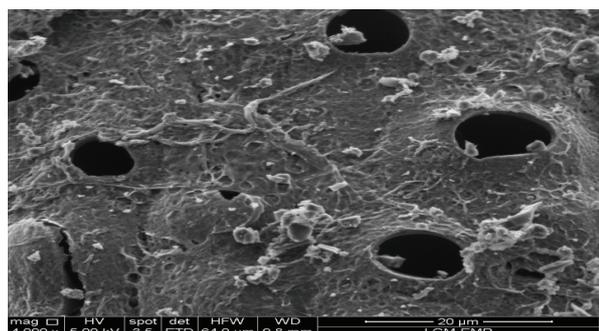


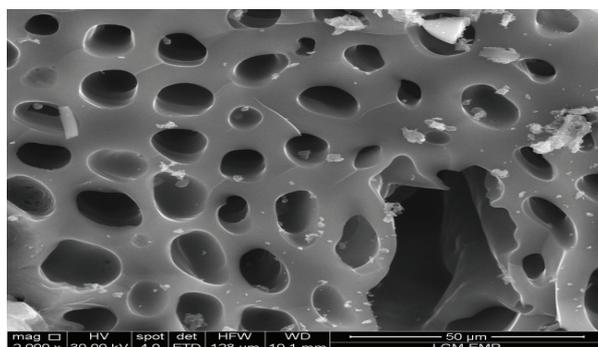
Fig. 4. FTIR spectra of ACGB, ACGE and ACMB.

the presence of an aromatic  $\nu_{\text{C}=\text{C}}$  ring stretching [20,44]. The entire band at 1,156, 1,146 and 1,139  $\text{cm}^{-1}$  indicates the  $\nu_{\text{C}-\text{O}}$  stretching vibrations in alcohols, phenols and ether groups and can also be assigned to vibrations of hydrogen bonds P–O to C–O to that of vibrations of bonds P–O–C (aromatic) and P–OOH or P–O–P result the interaction of the phosphoric acid with the molecule of the precursor, because  $\text{H}_3\text{PO}_4$  can be effectively removed completely by simply washing with water [45,46]. The weak bands at 1,058, 1,037 and 1,072  $\text{cm}^{-1}$  indicate the R–OH groups [47] or may be attributed to chemical bonding ionized  $\text{P}^+-\text{O}^-$  in the acid phosphate esters [48] and symmetric vibrations in strings P–O–P (polyphosphate) [45]. The bands between 2,354 and 2,363  $\text{cm}^{-1}$  signifying C–H stretching position  $<3,000 \text{ cm}^{-1}$  for saturated  $\text{CH}_3$ ,  $\text{CH}_2$  and CH of alkyls.

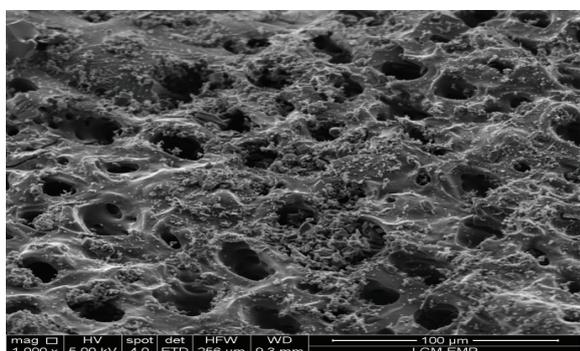
Scanning electron microscopy (SEM) technique was used to investigate the surface physical morphology of



(a)



(b)



(c)

Fig. 5. Scanning electron micrographs for the three varieties of activated carbon: (a) ACGB, (b) ACMB and (c) ACGE.

activated carbons [1]. It was seen from the micrographs of raw date stone (from our previous work [28]) that raw date stones is very flat with no cracks or any kinds of pores, looking very rigid and compact surface. The SEM micrographs of all the activated carbons ACMB, ACGB and ACGE in Fig. 5 show clearly well-developed pore structures.

### 3.4. Boehm titration

Boehm titration determined the functional groups on the surface of each activated carbon. These results listed in Table 2 indicated the predominance of the acidic characters of the carbonyl, phenolic or carboxylic functional groups. The highest total acidity titration was obtained at 2.8 meq/g. It is

to be noted that chemical activation involving phosphoric acid leads to the best results in terms of surface functionalization of the activated carbons.

## 4. Conclusions

Date stones are suitable for activated carbon production using phosphoric acid activation for activation temperature at 600°C for 3 h. The using of such activated carbons as adsorbents for organic and inorganic pollutants depends simultaneously on the nature of date stones variety and its origin. In this case, date stones coming from Biskera region seemed to be more workable than those coming from El-Oued ones. SEM micrographs show high porosity production compared with raw materials. The best surface area and micropore volumes for ACGB were, respectively, 1,118 m<sup>2</sup>/g and 0.52 cm<sup>3</sup>/g. According to D–R isotherm model, the calculated activation energy (4.28 kJ/mol) indicated that the adsorption kinetics is governed by a physisorption mechanism. In addition, the elucidation by FTIR of the functional groups nature may contribute considerably in the removal of emerging contaminants in water.

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## Abbreviations

ACGB	– Activated carbon of Ghers date variety of Biskra locality
ACGE	– Activated carbon of Ghers date variety of El-Oued locality
ACMB	– Activated carbon of Mech Degla date variety of Biskra locality
$P/P^0$	– Relative pressure
$S_{\text{BET}}$	– Specific surface area calculated from BET equation, m <sup>2</sup> .g <sup>-1</sup>
$S_{\text{ext}}$	– External surface area, m <sup>2</sup> /g
$S_{\text{micro}}$	– Micropore area, m <sup>2</sup> /g
$V_T$	– Total volume of pore, cm <sup>3</sup> /g
$V_{\text{micro}}$	– Micropore volume, cm <sup>3</sup> /g
$r_p$	– Pore radius = $2VT/S_{\text{BET}}$ , nm
$V_{\text{micro}}(D-R)$	– Micropore volume by D–R method, cm <sup>3</sup> /g
$L$	– Micropore size, nm
$E_0$	– Characteristic adsorption energy, kJ/mol
FTIR	– Fourier transforms infrared
SEM	– Scanning electron microscopy

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