

Article

High Surface Area Activated Charcoal for Water Purification

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Abstract: An activated charcoal with a high surface area of 4320–3800 m²/g with significant adsorption properties was prepared by the chemical and thermal processing of walnut residues. Iraqi walnut shells were sonicated with different ratios of potassium hydroxide (KOH). The mixture was then calcined at different temperatures using an electric oven until the best thermal conditions for a very high activated surface area and performance were identified. The resulting activated charcoal was further purified to remove residual KOH and metal impurities. Investigations revealed that the quality of the prepared activated charcoal was comparable to or surpassed that of commercially available counterparts in both the physical and adsorption properties. It was characterised for methylene blue degradation and the removal of heavy elements during water purification.

Keywords: charcoal; activated charcoal; walnuts; water purification; methylene blue degradation



Citation: Ahmed, A.S.; Alsultan, M.; Hameed, R.T.; Assim, Y.F.; Swiegers, G.F. High Surface Area Activated Charcoal for Water Purification. *J. Compos. Sci.* **2022**, *6*, 311. <https://doi.org/10.3390/jcs6100311>

Academic Editor: Thanasis Triantafillou

Received: 5 August 2022

Accepted: 12 October 2022

Published: 13 October 2022

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1. Introduction

Activated carbon (AC) is a porous carbonaceous material that is typically prepared from bio-organic substances. It first became important during World War I, when it was used in gas masks to adsorb toxic gases. Activated carbon is an amorphous form of carbon. It is usually prepared by the carbonation of certain raw materials such as wood, bones, coconut peels, and heavy oil residues. Generally, the activated carbon industry prefers the use of raw materials with a high carbon content [1–3].

Activated charcoal can be classified into two types according to its utilisation: granular AC that can adsorb toxic gases and harmful fumes such as phosgene and mustard gases, and industrial powder AC [4], which is used to bleach and remove colour from fats, oils, chlorin, sugar, organic fluids, pharmaceutical preparations, etc. [5].

In the field of gas adsorption, AC can be used to adsorb the fumes of ammonia gas, nitrogen dioxide (from combustion gases), carbon dioxide, methane, and hydrocarbon gases [5,6].

It is also used in the treatment of industrial water waste to remove chemicals as well as organic or inorganic pollutants. Other industrial applications include their use in carbon ion exchanges, for medical purposes, to adsorb odours from wounds and ulcers as well as for internal treatment for gas and toxins [7].

The most important application of activated carbon is the adsorption of materials from water medium, which is governed by two main types of force, namely physical and chemical adsorption. Some AC materials are inactive towards chemical adsorption due to electronic saturation of their surface atoms. Adsorption may then occur through the forces of natural attraction, which is known as ‘physio-adsorption’; examples include nitrogen adsorption on a silica surface and hydrogen adsorption on nickel metal. The forces that are responsible for such physical adsorption include dispersion and van der Waals forces, which are responsible for binding the adsorbed particles and adsorber or non-polar surfaces, which create additional forces called ‘polar diode interference’ [7,8].

In contrast, other surface atoms that have unsaturated electronic configurations prefer to form chemical bonds between the adsorbing surface and the adsorbed atoms or molecules. This type of adsorption is called chemical adsorption; examples include oxygen adsorption on activated charcoal, hydrogen chloride adsorption on an iron surface, and potassium or sodium adsorption on tungsten. Chemical adsorption depends not only on the porous composition of the charcoal material, but also on its chemical composition. The chemical composition has a significant effect due to variations in the crystal structure, which changes the electronic order and organisation of the carbon structure, resulting in unpaired electrons that control the adsorption of polarised and non-polarised materials [9].

Activated charcoal is often prepared from raw materials with various carbon compositions. Different chemical methods can be used to obtain charcoals with different adsorption properties. All such raw materials should contain a high starting carbon content. All chemical treatment processes must generally also include a carbonation reaction to remove the hydrogen atom bonded to the carbon atoms [2].

2. Materials and Methods

2.1. Materials

Activated carbon was prepared from walnut shells according to a procedure in the literature by using potassium hydroxide (the activated surface area was 1800 m²/g). Methylene blue (MB) dyes were provided by Sigma Aldrich Germany. The MB dye solution was prepared in a concentration of 20 ppm (0.04 g dissolved in 500 mL round bottom flask). Water samples were collected from different locations around the city of Mosul (Iraq).

2.2. Preparing the Raw Material

Dry walnut cores were milled and converted to powder form to create chemical interfaces. The walnut powder (10 g) was mixed with four different ratios of sodium hydroxide (wt powder: wt sodium hydroxide), namely, 0.25:1, 0.5:1, 0.75:1, and 1:1. After being thoroughly mixed, each mixture was soaked in water for 24 h and then heated to different annealing temperatures in the range of 300–600 °C in an electric oven over different annealing periods of time [9,10].

2.3. Activated Carbon Purification

After completing both the carbonisation and activation processes, the resultant activated charcoal samples were washed with water several times to remove all traces of sodium hydroxide/peroxide and any metal residues. The washing was continued until the pH of the washings was 7. The resulting activated carbon was dried overnight in air. Hydrochloric acid (10 mL of 0.1 N) was then added, followed by heating for 30 min with magnetic stirring to remove the remaining sodium ions. Thereafter, all samples were gently washed with distilled water several times to remove any hydrochloric acid that remained. The prepared samples were dried overnight and then stored under a dry, inert atmosphere [9,10].

2.4. Measurement of Charcoal Activated Surface Area: Iodine Number Measurement

Dry activated carbon (1 g) was weighed and placed in a 100 mL round bottom flask to which 10 mL of 5% HCl (vol 0.1 N HCl:100 mL distilled water) was added. The resultant solution was refluxed for 15 min to remove any organic substances that might interfere during the charcoal characterisation or application test. The solution was then left overnight to cool to laboratory temperature. Iodine solution (100 mL of 0.1 N) was thereafter added to the solution. The iodine solution was previously prepared by dissolving 12.7 g of iodine into 19.1 g of potassium iodide in a litre of water. The mixture was then shaken for 30 s and filtered. The first 20 mL of the filtrate solution was not used. The following 50 mL of the filtrate was calibrated with 0.1 N sodium thiosulphate solution that had been prepared by dissolving 24.8 g thiosulphate into 0.1 g sodium carbonate in a litre of distilled water. The calibration was continued until the mixture turned pale yellow. A few drops

of starch indicator were added into the mixture. The calibration sodium thiosulphate was added dropwise until the pale-yellow colour totally disappeared. The quantity of sodium thiosulphate calibration solution was recorded. The charcoal active area was calculated according to ASTM D4607-14 using Equation (1) below [11,12]:

$$IN = [A - (DF \times C \times B)]/m \quad (1)$$

where IN = iodine number, $A = 1269.3$ (molarity equation, $M = wt \times 1000/M.Wt \times V$), where $A = Wt$, C = the recorded burette volume after the pale-yellow colour disappears, B = the normality of the iodine solution multiplied by the atomic weight of iodine, $DF = 2.2$ correction factor value (which can be calculated from $100 + 10 = 110$ mL, while 50 mL was taken out for calibration process), and m = sample weight.

2.5. Measurement of Charcoal Activated Surface Area: Methylene Blue Dye Number Measurement

Dry activated carbon (0.1 g) was placed in a 50 mL round bottom flask and 50 mL of 20 ppm methylene blue dye dissolved in distilled water was added (0.02 g of the dye in 1 L of distilled water). The round bottom flask was shaken for 2 h in an electric shaker until the disappearance of the methylene blue colour. Another 50 mL of 20 ppm methylene blue solution was then added to the round bottom flask and shaking was continued for 2 h. This addition procedure was repeated until the methylene blue colour in the round bottom flask did not disappear. The total methylene blue concentration volume was recorded while the absorption of the activated carbon–methylene blue solution was measured with a spectrophotometer (Shimadzu UV-1800 Cole-Parmer company USA) at a 668 nm wavelength. Finally, the surface area of the activated charcoal was calculated using ASTM D2330-20 [13]:

$$Z = (y \times V)/1000 \quad (2)$$

where Z = the surface area; $y = 20 - X$, and y = total volume of methylene blue that absorbed, X = the concentration of total methylene blue volume when the colour of the charcoal solution was stable, the X value was obtained from the spectrophotometer standard absorption graph of concentration (x -axis) and absorption (y -axis), as shown in Figure 1.

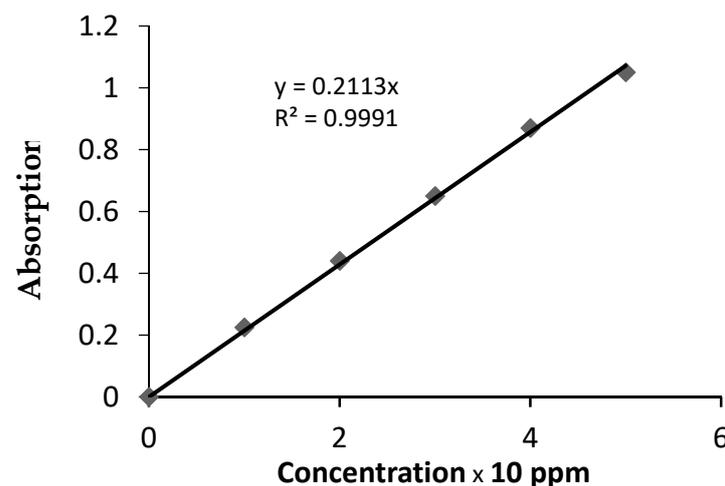


Figure 1. Standard absorption curve used to calculate the activated carbon active surface area.

2.6. Measurement of Charcoal Activated Surface Area: BET Method

An amount of activated charcoal was placed in a degassed vacuum system where the charcoal was exposed to nitrogen gas under various pressures. The adsorption of nitrogen gas was determined at standard conditions (STP). The active surface area was determined by measuring the amount of gas absorbed. A curve was plotted relating the pressure on

the *x*-axis to the amount of adsorbed gas on the *y*-axis. The resulting isotherm determined the adsorption type as well as the type of cracks and gaps on the charcoal surface [14].

2.7. Humidity Moisture Measurement

Dry activated carbon (1 g) was exposed to both air and atmospheric moisture for 24 h. The weigh change of the carbon was measured repeatedly, with the weight change corresponding to the humidity gained by the carbon. The percent humidity was calculated using the equation (ASTM D2247-15) [15]:

$$\% = (\text{primary weight before exposing to air and moisture}) / \text{weight of charcoal after exposure to air and moisture} \times 100$$

2.8. Ash Ratio Measurement

A ceramic lid containing 1 g of activated carbon was placed in an electric oven and heated to 1000 °C for 1 h. The weight of the ceramic lid was recorded again and the ash percentage was calculated using the equation (ASTM D2866-94) below [12]:

$$\% \text{ ash} = (\text{the difference between the weights before and after oven heated}) / \text{primary weight} \times 100$$

2.9. Atomic Absorption Measurements

The investigated samples were taken from different water sources around the city of Mosul in Iraq, and the percentage of heavy elements such as cobalt, lead, and dissolved ions, namely magnesium and potassium, was determined. All of the above samples were examined before and after treatment with the activated carbon to measure the absorption of these elements. CBC scientific equipment model 3175 was used to perform this test.

2.10. UV Measurements

Methylene blue (0.01 g) was added to 1 L of water to prepare 1000 ppm methylene blue dye. A total of 25 mL of the dye solution with 0.1 g of the activated carbon added was shaken for 5 min. A total of 99% of the methylene blue was removed. The process was repeated with 25 mL of 1000 ppm methylene blue dye and the removal rate of methylene blue was 90%. A SHIMADZU Model UV-1800 Spectrometer was used to process this characterisation.

3. Results and Discussion

3.1. Preparation and Characterisation of Activated Carbon

The activated carbon was prepared from Iraqi walnut shells using the procedure described in the Experimental section. Its physical properties were examined, with the results listed in Table 1.

Table 1. The physical and chemical properties of the prepared activated carbon (AC).

	BET (m ² /g)	IN (m ² /g)	Ash (%)	Humidity (%)
Physical properties data	4320	3943	0.245	11.33

The active surface area of the prepared AC was found to be 4320 m²/g by BET. To the best of our knowledge, this is the highest reported area for an AC; the previous best reported result in a peer-reviewed scientific publication was 3800 m²/g [16]. The surface area measured via IN was 3943 m²/g, which is close to the BET value.

Furthermore, the AC had a very low ash ratio of 0.245% while the humidity ratio was 11.33%. The SEM images (Figure 2) indicate a highly porous surface structure.

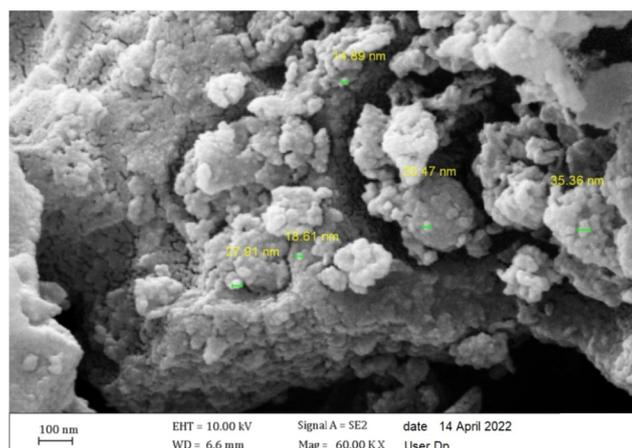


Figure 2. Scanning electron micrograph of the surface of the prepared activated carbon showing high porosity.

3.2. Absorption and Removal of Methylene Blue Dye from Water

Methylene blue (MB) is a heterogenous aromatic compound belonging to the thiazine family, with significant adsorption properties. It has found application in studies of organic contamination and colour removal agents from liquid solutions. Table 2 lists its chemical and physical properties.

Table 2. The physical and chemical properties of methylene blue (MB).

Property	
Family	Thiazine (basic dye)
Chemical formula	$C_{16}H_{18}N_3SCl$
Scientific name (IUPAC)	3,7-bis-(dimethylamino)phenazathionium
Molar mass	319.85 g/mol
Colour point remark number (CI)	52,011
Maximum absorbance wavelength	665 nm
Chemical structure formula	

Figure 3 illustrates the calibration curve of MB adsorption at different standard concentrations (20, 40, 60, 80, 100 ppm). The resulting absorption equation was $y = 0.2113x$ (where y = absorbance value and x = the MB concentration) with a correlation value (R^2) of 0.9996. The equation was derived as per the Beer–Lambert law [17,18].

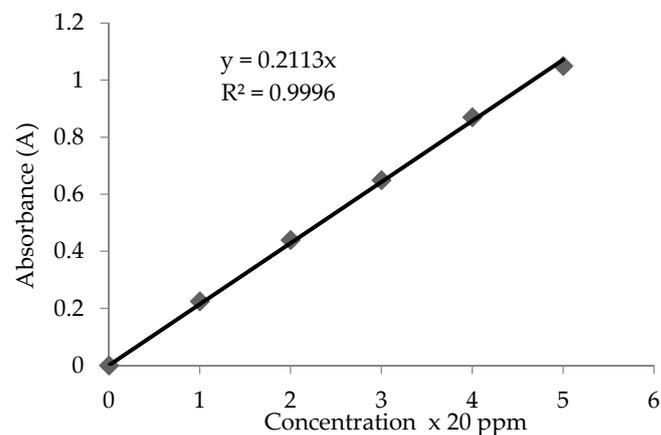


Figure 3. Calibration curve of MB absorption.

Table 3 shows the data for the activated charcoal (AC) as an adsorption and removal agent of MB dye, with 6.0 ppm as the primary concentration before AC absorption (Column marked 'MB' in Table 3). As can be seen in the columns marked '1' (single application of AC), '2' (double application of AC), and '3' (triple application of AC), the concentration of MB was reduced from 6 to 0.184 ppm after three applications. Figure 4 summarises the change in the MB concentration. The AC removal efficiency of MB reached up to 96.93%.

Table 3. Removal of methylene blue (MB) from 10 mL of a water solution by sequential applications of 0.1 g of the activated carbon (AC) (in the order '1', '2', and '3'; the right-most column shows the data from a control water sample).

Symbol	MB	1	2	3	H ₂ O
MB conc. in ppm	5.579	1.344	0.307	0.184	0.042
UV-Abs.	1.176	0.284	0.092	0.039	0.009

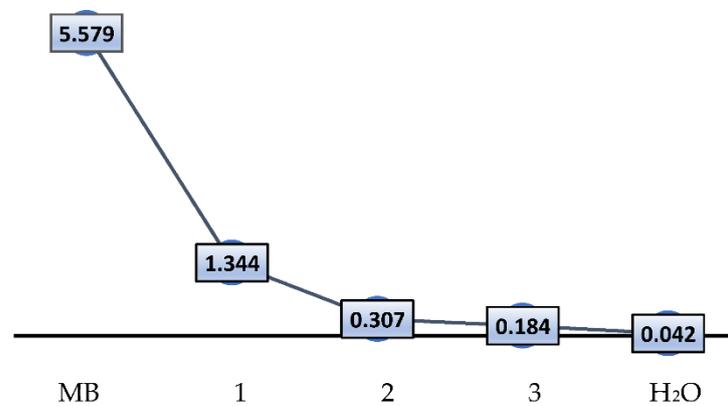


Figure 4. Decline in methylene blue (MB) concentration (in ppm) as listed in Table 3.

The bottom row of Table 3 represents the UV–Vis absorbance of each MB solution. The absorbance was reduced from 1.176 to 0.009. The blue dots in Figure 5 represent these results overlaid on the calibration curve. As can be seen, the data followed the curve as per the Beer–Lambert law with the correlation $R^2 = 0.994$.

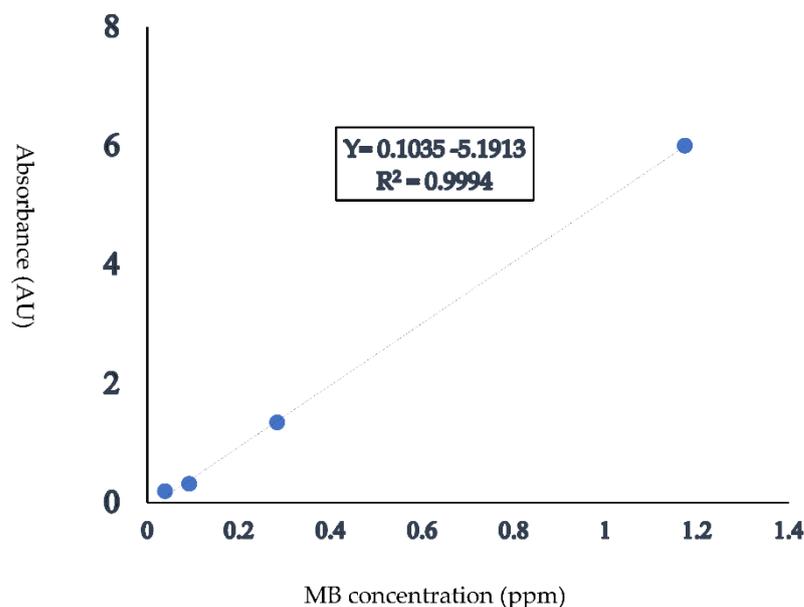


Figure 5. UV–Visible absorption of the samples in Table 3 (blue dots), overlaid on the calibration curve of MB (black line). Concentrations on the x-axis are given in ppm.

It was observed that the MB solutions turned totally colourless in going from the original MB sample ('MB') after a single application of AC ('1'), double application of AC ('2'), and triple application of AC ('3') (Figure 6).

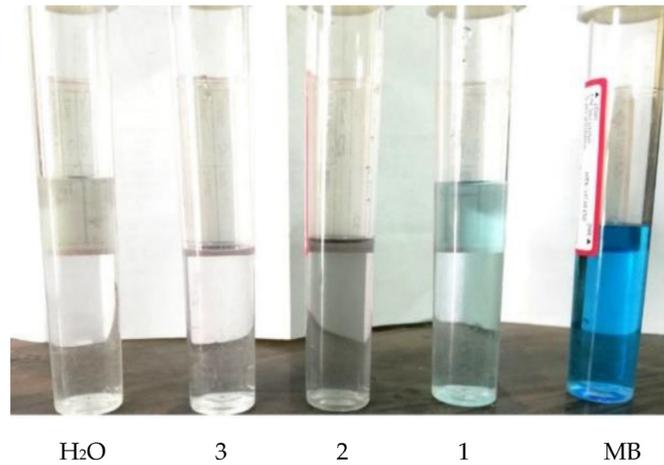


Figure 6. Photographs of the solutions in Table 3.

Consequently, as can be seen in Figure 7, the UV–Vis absorbance peak intensity reduced from 5.579 ('MB') to 0.184 ppm (peak 2) due to extremely AC absorbance activity. As above-mentioned, AC removed MB by 96.93% and the broad absorbance peak was almost removed.

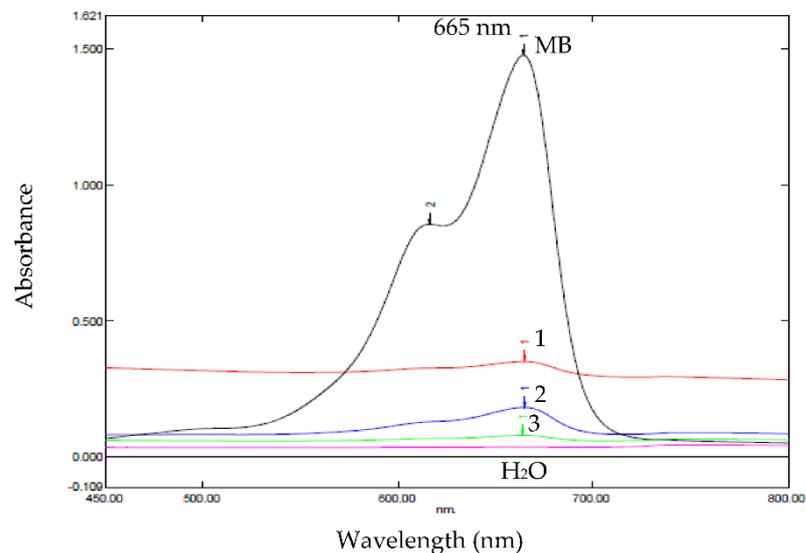


Figure 7. UV–Visible absorbance curves from the highest to lowest MB concentration (in ppm). The highest concentration of MB was 6 ppm, while 1, 2, and 3, represent the absorbance peak after the first, second, and third application of 0.1 g of AC.

Heavy Element Absorption

Five samples of wastewater were collected from locations around the city of Mosul, Iraq, to investigate lead (Pb) contamination. The locations were: Alkhossar wastewater, deep well in east Mosul, deep well in west Mosul, an industrial battery treatment workshop area, and a sulphur underground water spring (in the east of Mosul).

Typical activated carbon (0.1 g) was added to 10 mL of each sample and the Pb concentration before and after water treatment via AC adsorption was determined using atomic adsorption (with a calibration curve of Pb in the ppm concentration range) [19–21].

Table 4 shows the Pb concentration of each sample before and after AC absorption. As can be seen, the Pb removal was 93% on average.

Table 4. Description of the physical and chemical properties.

Symbol	Wastewater	Mosul East Well	Mosul West Well	Batteries Workshop—Washing Area (Waste)	Natural Spring Water (East Mosul)
Pb conc. (ppm; before AC treatment)	6.00	0	0	2.000	1.00
Pb conc. (ppm; after AC treatment)	0.43	0	0	0.153	0.07

4. Conclusions

A novel activated carbon (AC) with a record high unit surface area was prepared by a chemical approach from Iraqi walnut shells. A variety of techniques were used to characterise its properties including iodine number (IN), BET, humidity—moisture and ash ratio measurements, UV–Visible absorption, atomic absorption, and scanning electron microscopy (SEM). The results confirmed that the AC has what is believed to be the highest surface area per unit weight yet recorded, giving it powerful pollutant removal capacities when cleaning wastewater. The BET and iodine number investigations indicated surface areas of 4320–3800 m²/g. When applied in heavy element removal such as Pb removal, it was proven to be highly effective. It also readily removed the organic dye methylene blue. The AC removed 96% of the Pb contaminant, while the MB colour removal reached almost 94%.

Author Contributions: A.S.A. and R.T.H.; methodology, M.A.; validation, formal analysis, and investigation, Y.F.A.; resources, and data curation, G.F.S.; writing—original draft preparation, writing—review and editing, visualization, supervision, A.S.A.; project administration. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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