Pyrolysis of grape bagasse to produce char for Cu(II) adsorption: a circular economy perspective

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Abstract
Based on cleaner production and circular economy concepts, chars were produced through thermochemical conversion of grape bagasse and then used as adsorbents to uptake Cu(II) from aqueous media since Cu(II) is a common element found in fungicides to treat grapevines. The grape bagasse and char characteristics were investigated through several analytical techniques (TGA, SEM, XRD, FTIR, and BET). Three chars were obtained using different pyrolysis temperatures: 700, 800, and 900 °C. The materials had similar removal percentages and adsorption capacity. The char produced at 700 °C was chosen due to its lower production cost. Studies were conducted on the adsorbent dosage and pH effect, adsorption kinetics, isotherms, and thermodynamics. The most efficient dosage was 1.5 g L\(^{-1}\), and the pH was 5.5. The kinetic study showed that the equilibrium was reached in 60 min and the pseudo-second-order model presents the best fit. After the temperature influence study (25, 35, 45, and 55 °C), it was possible to verify that Cu(II) adsorption through char was favored at 55 °C. The Freundlich model showed the best fit for the experimental data. The highest removal percentage was 96.56%, and the high maximum adsorption capacity was 42 mg g\(^{-1}\). The thermodynamic study shows the adsorption as a spontaneous process, favorable, and endothermic.

Keywords Adsorption · Char · Cu(II) · Grape bagasse · Pyrolysis

1 Introduction
Recently, in the Organisation Internationale de la Vigne et du Vin (OIV) report, wine production was described as one of the most important agro-industrial activities in the world [1]. Wine production is an important part of the agriculture and beverage industry worldwide. Grape wine represents one of the most important alcoholic beverages globally, with continuously growing demand [2]. For this reason, grape production is one of the largest activities globally, with around 50 million tons produced every year [3]. In 2016, 75.7 million tons of grapes were produced worldwide [4, 5]. Newly, in 2019, 84.8 million tons were produced, as registered by OIV. Although many grape-based food products can be found on the market, studies showed that about 75% of world production is destined for the wine industry [3]. According to Beres et al. [3], 1 kg of grape is required to produce 0.75 L of red wine, and it is estimated that global wine production is around 27 billion liters per year [5]. Unfortunately, this high production is associated with a lot of waste [4].

During wine production, about 25% (in weight) [4] of the grape results in residues, called bagasse [6]. This biomass is heterogeneous and composed of stalks, grape skins, and seeds [5, 7]. For the production of 100 L of wine, 18 kg of grape bagasse is generated, and therefore, around 5 million tons of this residue are generated annually worldwide [8]. This large amount of waste has been documented as one
of the most important problems facing the wine industry [9]. However, the use of this residue for composting cannot provide a full solution because of the enormous quantities of land required for this disposal [4]. In addition, large amounts of bagasse are produced during a short harvesting period, which increases the concentration per area [3, 6, 9]. In the same way, neither winemaking wastes are used as a fertilizer due to their high organic content: the salts and their acidity can negatively affect plant growth [4]. Furthermore, incineration or discard in the land field can be harmful to the environment due to the phenolic compounds decreasing pH of the pomace and increasing resistance to biological degradation [3]. Furthermore, this residue presents high moisture and nutrient contents that cause bacterial growth and uncontrolled emission of greenhouse gases [1].

Traditionally, grape bagasse has been used to obtain alcohol, food coloring, and grape seed oils. More recently, some research has focused on producing other value-added products, such as extracts of bioactive compounds, mainly phenols, tartaric acid recovery, and flour manufacturing. However, the most common functions associated with bagasse are antioxidants, followed by fortifying agents, dyes, and antimicrobials. These products were mainly applied in the preparation of meat and fish products and, to a lesser extent, in cereal products [10]. At the same time, the use of these residues for adsorption purposes is promising, considering that agricultural materials contain proteins, polysaccharides, and lignin, which are associated with functional groups responsible for the adsorption of metal ions, for example. According to Chand et al. [11], the abundant natural occurrence and many functional groups on the surface characterize several agricultural residues as good alternatives for synthesizing adsorbents, which can replace conventional materials.

In the last years, interest has increased in developing low-cost adsorbent materials using agricultural by-products or agro-industrial waste [12–15]. These materials are abundant, easily available, and inexpensive, which justify and enable various research [12, 13]. Furthermore, the wine industry is urgently asking for alternatives to manage its large amount of waste as raw material, so many works have been developed to produce adsorbents from this agro-industrial residue [5].

Char is a charcoal-like material derived from thermal processing (e.g., pyrolysis) of carbon-rich biomass (e.g., forest and agricultural waste, industrial by-products and waste, raw materials) [13, 16, 17]. In this sense, the grape bagasse can be converted into char through this thermochemical conversion called pyrolysis. Pyrolysis is characterized by the degradation of organic matter in the total or partial absence of oxygen. It results in three by-products: solid (char), liquid (bio-oil), and gaseous (non-condensable gases) [15, 18, 19]. Each of these fractions can be applied in different areas, depending on their properties. The bio-oil contains hundreds of organic compounds such as alkanes, aromatic hydrocarbons, phenol derivatives, and little amounts of ketones, esters, ethers, sugars, amines, and alcohols [5, 20]. Generally, bio-oils can produce chemicals like food flavorings, resins, fertilizers, and emission control agents [20] and as feedstock to produce energy [5, 21]. The non-condensable gases consist mainly of hydrogen (H2), carbon dioxide (CO2), carbon monoxide (CO), propane (C3H8), and methane (CH4) [21]. They have a low to medium heating value but may contain sufficient energy to supply the energy requirements for utilization through pyrolysis [5, 20]. Due to the high temperatures used in the pyrolysis process, which remove the moisture and volatile matter content from the biomass, the resulting char has different properties. The main differences are porosity, specific surface area, pore structure (micropores, mesopores, and macropores), and physicochemical properties such as composition, ultimate analysis, and ash content [22]. The porosity of chars is dependent on pyrolysis temperature, and it has been shown that higher temperatures could lead to a larger pore size [21]. These changes in properties generally increase the material’s reactivity and, therefore, one of the possibilities for using the char obtained is as an adsorbent material [22]. Due to their unique properties (large surface area, high porous structure, surface-enriched functional groups, affinity towards metals, stability, and the presence of certain mineral components), materials such as chars are effective in removing heavy metal contaminants from wastewater [13, 14, 17, 23]. Chars then can be used as a substitute for activated carbon, for example [24, 25].

The chars obtained are applied in the adsorption process, a technique widely useful in environmental remediation to control water and air resource pollution [24]. Adsorption is the phenomenon of mass exchange by which the material is moved from the fluid stage to the surface of a solid and bound by chemical and physical interactions [17]. Adsorption methods can be an attractive alternative in the removal of pollutants from contaminated waters [12], owing to their various pros such as operation with adsorbents derived from agricultural and industrial wastes, cost-effectiveness, higher efficiency, a wide selection of established, and low energy requirements [17]. Furthermore, the adsorption process is an effective and economical method for Cu(II) removal from water, as it is the simplest and cheapest alternative [26]. Moreover, this process presents flexibility in design and operation and can deliver high-quality treated effluents and wastewater [27].

It is a fact that heavy metals are very dangerous for the entire ecosystem and industrial growth introduced enormous levels of them into water resources in recent years [28, 29]. These metal ions are released into the environment by various industrial processes that contaminate the environment by releasing effluents [17, 23]. Aquatic environments, especially groundwater and rivers, are the primary transport medium for
these metals [16]. Therefore, it is essential to treat metal-polluted wastewater before its release into the environment [29]. Copper, zinc, and mercury are some of the metals commonly found in industrial effluents [17, 27]. Excess concentrations of these metals in the water are related to diseases in the liver and kidneys and affect the nervous, gastrointestinal, and hematopoietic systems [17, 27]. Most often, they are carcinogenic [29]. Cu(II) ions, toxic to the environment and human life [30], are related to gastrointestinal problems, mucosal irritation, kidney damage, depression [26], lung cancer, abdominal pain, diarrhea, liver toxicity, and weakness [29]. These heavy metals are among the most important water pollutants due to their important characteristics: non-degradability, toxicity, and bioaccumulation tendency, which facilitate their inclusion and long persistence in the food chain [12, 28].

The scientific contribution of this work is the development of a study on the treatment and reuse of grape bagasse (waste generated in the processing of grapes for the production of juices and wines), transforming it into chars. The grape residue and its char were adsorbents to remove Cu(II) ions from solutions. The choice of Cu(II) ions was made considering that compounds containing Cu(II) ions, such as copper hydroxide, are recommended and used to treat grapevines, like fungicide, representing an environmental problem. Therefore, this work contemplates applying cleaner production and circular economy concepts in the wine sector.

2 Materials and methods

2.1 Grape bagasse: collection, preparation, and characterization

The grape bagasse used in this study was provided in a rural property located in Dois Lajeados, the Rio Grande do Sul, Brazil. In this region, the climate is defined as Cfb (temperate oceanic climate), with temperate summer, according to Koppen’s climate classification [31]. The average temperature is 17.2 °C, the coldest month averaging above 0 °C, and all months with average temperatures below 22 °C. First, the material was dried at 80 °C for 48 h and milled in a knife mill to obtain a sample with particle sizes lower than 0.5 mm (mesh 35). Then, in the adequate particle size, the characterization analysis was conducted. The grape bagasse was characterized by ultimate analysis (CHNS), proximate analysis, main components, high heating value (HHV), and thermogravimetric analysis (TGA). The ultimate analysis was carried out in an Elemental Analyzer (brand Elementar, model Vario Macro Cube). According to the American Society for Testing and Materials, the proximate analysis (moisture, volatile matter, ash, and fixed carbon) was conducted (ASTM D1762-84). The Van Soest modified method determined cellulose and hemicellulose components [32]. To determine lignin, the method TAPPI T222 om-02 was used. The method ASTM D5865-04 with a calorimetric pump (brand IKA, C-200) was employed for HHV determination. Finally, the thermogravimetric analysis was conducted in a Netzsch thermogravimetric balance (model STA 449 F3 Jupiter) starting from room temperature until 800 °C, using a heating rate of 25 °C min⁻¹ with an N₂ flow of 50 mL min⁻¹.

2.2 Pyrolysis of grape bagasse

The pyrolysis experiments of grape bagasse were conducted in a horizontal tubular reactor under different conditions. Previous work reported all the specifications of the pyrolysis apparatus [33]. Figure 1 shows a representation of the pyrolysis process used for char production.

A total of 100 g of grape bagasse (previously dried) was inserted into the reactor. Three temperatures of pyrolysis were investigated: 700, 800, and 900 °C. A holding time of 60 min was used for all of these temperatures. The inert gas utilized was N₂ in a flow of 0.2 L min⁻¹, and the heating rate employed was 5 °C min⁻¹.

Three products were obtained through this pyrolysis process: char, bio-oil, and non-condensable gas. The fraction of condensable vapors formed by pyrolysis was collected in a sequence of 10 bubblers in a refrigerating system (about −10 °C). Each bubbler contained 100 mL...
of isopropyl alcohol, except for the first and last. All the bubblers were weighed before and after each experiment. The non-condensable gas was collected during the pyrolysis using a trap. A gas meter was placed close to the trap to measure the volume of gas formed. Three chars were obtained according to the pyrolysis temperature used: C700, C800, and C900. These chars, after characterizations, were used in the adsorption processes of Cu(II).

2.3 Characterization of the pyrolysis products

The yield of each fraction produced in the pyrolysis process was analyzed according to the temperature applied. The non-condensable gas was characterized by gas chromatography (GC) (brand Dani Master) with a thermal conductivity detector. The separation was carried out in a Carboxen™ capillary column (30 m long × 0.53 mm internal diameter × 30 µm film thickness) (brand Supelco, model 1006). The calibration curves were obtained using gas standards.

The grape bagasse and the chars produced were characterized by scanning electronic microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). The SEM images were obtained using a microscopic model MIRA 3 (brand Tescan). The structural characteristics of the materials were determined by the XRD technique, using an equipment model MiniFlex 300 (brand Rigaku). The analysis conditions used were as follows: radiation of Cu Kα (λ = 1.54051 Å) and power supply with 30 kV and 10 mA mode step (with scan speed of 0.5 s and scan step of 0.03°), in angles of 5 to 100°. FTIR analysis was conducted to identify the main functional groups of the materials using a spectrophotometer model IR Prestige (brand Shimadzu). The method used direct transmittance of KBr pellets. The spectra were obtained in the 400 to 4500 cm⁻¹, and 45 scans were performed at a resolution of 2.0 cm⁻¹. The char’s specific surface area, pore size, and pore volume were obtained through adsorption/desorption isotherms of N₂. The Brunauer–Emmett–Teller (BET) pore volume were obtained through adsorption/desorption using a thermal conductivity detector. Desorption was separated from the aqueous solution by centrifugation (LGI-DLC-802B, LGI Scientific, Brazil), and the concentration of Cu in the supernatant was analyzed by atomic absorption spectrometry (AAS), model 240 FS AA (brand Agilent Technologies). The Cu(II) analysis was performed by flame emission, using flame stoichiometry oxidizing (fuel acetylene and support air). After the experiments, the adsorbent was separated from the aqueous solution by centrifugation (LGI-DLC-802B, LGI Scientific, Brazil), and the concentration of Cu in the supernatant was analyzed. The calculation of adsorption capacity (adsorbed quantity of Cu(II) per mass unit of adsorbent) and the Cu(II) removal percentage removal are given by Eqs. (1) and (2) respectively.

\[
q = \frac{C_0 - C}{m} V \quad (1)
\]

\[
\%R = \left(\frac{C_0 - C}{C_0}\right) \times 100 \quad (2)
\]

where \(C_0\) and \(C\) are the initial and final concentrations of Cu(II) ions (mg L⁻¹), respectively, \(m\) is the mass of adsorbent (g), and \(V\) is the volume of solution (L).

- **Effect of adsorbent type:** To define the best adsorbent between GB, C700, C800, and C900, these materials were introduced in a 1.5 g L⁻¹ with 50 mL solution of 30 mg L⁻¹ Cu(II) (at pH 5, using H₂SO₄ 0.1 mol L⁻¹). The Erlenmeyer flasks were placed in a shaker (SL222, Solab, Brazil) at 25 °C operating at 150 rpm to agitate the mixture for 3 h.
- **Adsorbent dosage effect:** Experiments were conducted using six different dosages (from 0.25 to 1.5 g L⁻¹) to evaluate the dosage effect.
- **pH effect:** The pH effect was evaluated from 1 to 6 (considering that Cu(II) precipitates at pH 6).
- **Kinetics:** The effect of the contact time on Cu(II) adsorption capacity was investigated from 0 to 180 min at initial Cu(II) concentrations of 30, 50, 80, 120, and 200 mg L⁻¹.
- **Isotherms:** To investigate the effect of temperature on char adsorption capacity in Cu(II) solutions, four temperatures were used: 25, 35, 45, and 55 °C, with different initial concentrations of Cu(II) (\(C_0\)): 0, 30, 50, 80, 120, and 200 mg L⁻¹.
- **Desorption:** Desorption experiments were carried out to investigate the possibility of reusing the chars. For this process, three different acids (HClₐq, HNO₃ₐq, and H₂SO₄ₐq) were tested at two different concentrations: 0.2 and 0.5 mol L⁻¹.

2.4 Experimental studies of Cu(II) adsorption

The materials GB, C700, C800, and C900 were used in adsorption experiments of Cu(II). A stock solution of 1 g L⁻¹ CuSO₄·5H₂O was prepared, and all the experiments were carried out by diluting this one. The Cu(II) concentration was determined through atomic absorption spectrometry (AAS), model 240 FS AA (brand Agilent Technologies). The Cu(II) analysis was performed by flame emission, using flame stoichiometry oxidizing (fuel acetylene and support air). After the experiments, the adsorbent was separated from the aqueous solution by centrifugation (LGI-DLC-802B, LGI Scientific, Brazil), and the concentration of Cu in the supernatant was analyzed. The calculation of adsorption capacity (adsorbed quantity of Cu(II) per mass unit of adsorbent) and the Cu(II) removal percentage removal are given by Eqs. (1) and (2) respectively.

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2.5 Cu(II) adsorption modeling

The Cu(II) adsorption modeling was carried out through kinetics, isotherms, and thermodynamic calculations. First,
pseudo-first-order and pseudo-second-order models were implemented to study the Cu(II) adsorption kinetic curves [34, 35]. Second, Langmuir and Freundlich’s models were used to describe Cu(II) adsorption [36, 37]. Third, the adsorption modeling and interpretation were based on Piccin et al. [38], Dotto et al. [39], and Dotto and McKay [24]. Finally, the adsorption thermodynamics was evaluated using Gibbs free energy change, enthalpy change, and entropy change [40]. Details can be found in the Supplementary Material.

3 Results and discussion

3.1 Grape bagasse characteristics

Table 1 shows the main characteristics of the grape bagasse used. The ultimate analysis shows that GB is mainly composed of carbon, oxygen, and hydrogen, like most lignocellulosic materials [41]. Besides, the proximate analysis results presented that GB has 72.98% wt. of volatile matter and 4.02% wt. of ash. This high value of volatile matter and low ash value is favorable to the thermochemical conversion process [42].

The proportion of cellulose, hemicellulose, and lignin of biomass, such as GB, can vary from one plant species to another, according to age growth stage, among other conditions [44]. Nevertheless, similar cellulose, hemicellulose, and lignin values were recently reported by Mortari et al. [43]. Higher lignin content in biomass is associated with higher char yield by pyrolysis (while higher cellulose or hemicellulose content is related to simpler thermal or chemical modifications to induce functional groups) [17]. Lignin is a macromolecule with a complex structure. When it is thermally decomposed at high temperatures, it forms free radicals of phenol through re-polymerization and condensation reactions that result in solid residues (char). Therefore, cellulose and hemicellulose are easily decomposed because they have simpler structures [45].

The HHV of a material is the expression of the energy content released when burnt in the air [42] and is related to the concentration of C and H. For example, the HHV value for GB is 21.79 MJ kg⁻¹ and is related to the percentage of C and H, which are 50.6 and 7.42 wt.%, respectively.

The GB sample was subjected to thermogravimetric analysis to determine the general decomposition characteristics. In the thermogram (Fig. 2), the weight loss observed from 50 to 200 °C is due to moisture loss and volatile organics. The main weight loss observed between 200 and 500 °C can be attributed to the decomposition of hemicellulose, cellulose, and lignin [46]. The literature reports that the decomposition of hemicellulose and cellulose occurs between 180 and 240 °C, respectively, while lignin decomposition occurs between 180 and 750 °C [41].

The FTIR spectrum of GB is shown in Fig. 3. The band in 3421.86 cm⁻¹ is attributed to O–H bonds in the functional group’s alcohols, phenol, or carboxylic acid [15, 26] in lignin, cellulose, and hemicellulose structures [47]. The bands in 2925.17 and 2855.73 cm⁻¹ are assigned to the stretching vibrations of C-H bonds [26] of the aliphatic and aromatic groups that form the main components of GB: cellulose, hemicellulose, and lignin. The band at 1746.61 cm⁻¹ refers to the carbonyl group (C = O) [26], which indicates the presence of polysaccharides, such as hemicellulose [47] and phenol carboxylic acids [48]. The band at 1615.45 cm⁻¹ can be assigned to the C = C bonds of the aromatic ring of the lignin [15], and C = O is present in carbonyl groups of

| Table 1 | Characteristics of grape bagasse | Literature |
|---------|---------------------------------|------------|
|         | **Main characteristics of the grape bagasse** | **Literature** |
|         | **Ultimate analysis (wt.%)** | | |
| C       | 50.60 ± 0.001 | 46.59 [20] |
| H       | 7.42 ± 0.13 | 6.25 [20] |
| N       | 2.16 ± 0.08 | 1.67 [20] |
| S       | 0.29 ± 0.0005 | 0.16 [41] |
| Oa      | 39.54 ± 0.21 | 45.49 [20] |
| **Proximate analysis (wt.%)** | | |
| Volatile matter | 72.98 ± 0.20 | 68.42 [20] |
| Ash     | 4.02 ± 0.11 | 4.70 [20] |
| Fixed carbon | 19.10 ± 0.47 | 20.68 [20] |
| Moisture | 3.89 ± 0.30 | 6.20 [20] |
| **Chemical composition (wt.%)** | | |
| Cellulose | 3.94 ± 0.95 | 5.70 [43] |
| Hemicellulose | 12.37 ± 1.70 | 9.20 [43] |
| Lignin | 41.51 ± 1.38 | 42.40 [43] |
| **High heating value (MJ kg⁻¹)** | | |
| HHV     | 21.79 | 21.20 [43] |

*aCalculated by difference

![Fig. 2 TG and DTG thermograms of GB](image)
aldehydes and ketones that form the lignin structure [15, 49]. The C-O stretching at 1071.50 cm⁻¹ can confirm the lignin structure [48]. XRD was used to obtain information about the crystallinity of the material. The XRD (Fig. 1S) patterns confirm a typically amorphous structure.

It is possible to evaluate the morphology of the GB surface through the images obtained by SEM (Fig. 4), which indicate the presence of particles of different shapes and sizes. According to the literature [48, 50], the GB is irregular, and the absence of porosity is apparent. Thus, the heterogeneous surface of this material is related to its composition of different parts of the fruit.

### 3.2 Pyrolysis yields

The yields of the fractions obtained from GB pyrolysis are presented in Fig. 5. The increase in temperature causes a decrease in the yield of char (from 32.30 to 30.65% wt.) and a consequent increase in the production of non-condensable gases (from 23.44 to 30.91% wt.). This fact is reported in the literature [20] since high temperatures increase recombination and cracking secondary reactions, favoring the formation of volatile fractions.

### 3.3 Non-condensable gases characteristics

The non-condensable gases produced during the GB pyrolysis experiment were collected and analyzed according to the pyrolysis temperature. The gas collections were carried out during the non-isothermal and isothermal regions. Figure 6 presents the main composition of the non-condensable gases obtained through gas chromatography.

It is possible to observe that for the three investigated temperatures (700, 800, and 900 °C), the main gas obtained was hydrogen gas. The average concentration of this gas was 78.08 (%vol.) for the temperature of 700 °C, 67.45 (%vol.) for the temperature of 800 °C, and 72.76 (%vol.) for the temperature of 900 °C. The high production of $\text{H}_2(\text{g})$ can be attributed to the rupture and deformation of the $\text{C} = \text{C}$ and $\text{C-H}$ bonds present in the aromatic rings that compose the GB structure and the cyclization and cracking processes of the primary pyrolytic vapors [43]. In the pyrolysis process, the lignin is responsible for producing $\text{H}_2(\text{g})$ and $\text{CH}_4(\text{g})$, the cellulose is responsible for producing high concentrations of $\text{CO}(\text{g})$, and the hemicellulose produces $\text{CO}_2(\text{g})$ [51].
3.4 Char characteristics

The FTIR spectra in Fig. 7 show the main functional groups present in char surfaces. It is possible to compare with the FTIR spectrum obtained for GB (Fig. 3). It is possible to verify the vanishing of some functional groups found in the GB before the pyrolysis. In addition, it can verify that the increase in temperature did not cause significant changes in the functional groups present in the materials since the chars have similar bands. Nevertheless, a change in the intensity of the bands was observed, which is attributed to the volatilization reactions that occur during pyrolysis. The band in 3429.58 cm\(^{-1}\) can be attributed to O–H bonds of alcohol, phenols, or carboxylic acid groups [52, 53]. The band observed in 1650.17 cm\(^{-1}\) can be assigned to the C = C stretching vibration in the char structure [52]. The band in 1392.66 cm\(^{-1}\) is assigned to the C-N bonds of amides or amines or C-H bonds [54]. At last, the band at 1036.78 cm\(^{-1}\) might be assigned to the stretch vibrations of C-O bonds of carboxyls, alcohols, and phenols groups [14].

The XRD patterns presented in Fig. 8 confirm a typically amorphous structure. Thus, according to the literature [55], the volatile organic compounds are eliminated during the pyrolysis process, and the char originated remains like a product with an amorphous structure.

SEM technique was used to assess the surface morphology of the chars. When comparing the SEM images obtained for the chars (Fig. 9) with the GB microscopies (Fig. 4), significant differences in the surface of the materials can be observed. These differences indicate that the decomposition reactions started producing and releasing volatile matter, forming pores, voids, and empty spaces (evidenced through the pore distribution analysis present in Fig. 10).

The N\(_2\) adsorption/desorption isotherms (BET) and pore size distribution (BJH desorption) of chars are shown in Fig. 10. According to the IUPAC classification, the C700 isotherm is type V, with H3 hysteresis, and the other isotherms (C800 and C900) are type IV, with H4 hysteresis. Type IV
and type V isotherms are usually observed for mesoporous adsorbents, such as chars. Therefore, the classification of the type of the adsorption isotherm can provide preliminary qualitative information about the adsorption mechanism and the porous structure of the chars. Furthermore, through the figures, it is also possible to observe the pore size distribution, which corroborates with the average pore size.

Table 2 shows the textural properties of the materials. The increase in total pore volume and the specific surface area of chars occurs according to the temperature increase. According to Machado et al. [55], Shen et al. [56], and Agrafioti et al. [57], the temperature increase can lead to the degradation of the main components of the biomass, resulting in a larger formation of pores in the char and an increase in the specific surface area. Zhao et al. [15] presented that the pyrolysis temperature was the most influential parameter affecting the char surface area. Volatiles released as gases at higher pyrolysis temperatures were found to generate pores [58]. Regarding the average pore size, the chars produced can be classified as mesoporous (2 to 50 Å) according to IUPAC. This classification can induce the materials to be used as adsorbents in the liquid phase.

The last feature evaluated for the chars was the point of zero charge (pH_{ZPC}). The eleven points experiment [24, 25] was used to find the pH_{ZPC} values. The results revealed that for all chars, pH_{ZPC} ranged from 6.98 to 7.05, with no significant difference at 95%. We can then conclude that the chars are negatively charged at solution pH values higher than 7. On the other hand, they are neutral at a pH of around 7. Finally, the chars are positively charged at pH values lower than 7.

### 3.5 Cu(II) adsorption: effects of adsorbent, dosage, and pH

Initially, a comparative Cu(II) adsorption experiment was carried out between GB and the three chars produced (C700, C800, and C900), using an initial Cu(II) concentration of 30 mg L\(^{-1}\) and an adsorbent dosage of 1.5 g L\(^{-1}\) at pH 5. Figure 11 shows the removal percentage values and adsorption capacities.

It can be seen that all chars presented better performances than the precursor GB; i.e., the chars could remove more than 95% of Cu(II) from the solution with an adsorption capacity of around 20 mg g\(^{-1}\). On the contrary, GB has removed only 5% with an adsorption capacity of around 2 mg g\(^{-1}\). These results indicated that the pyrolysis process is suitable for transforming the grape bagasse into effective adsorbents (chars). Another important fact is that C700, C800, and C900 presented similar adsorption results for Cu(II). Even though the pyrolysis temperature improved the surface characteristics (Table 2), this behavior occurred. In this way, the Cu(II) adsorption may depend on similar functional groups. Therefore, it is possible to define the char produced at 700 °C (C700) as the most suitable adsorbent for removing Cu(II) from an aqueous solution since this material can be produced at a lower temperature, representing a relatively low operation cost.

Afterward, assays were carried out to determine the most suitable adsorbent dosage. The most efficient dosage for Cu(II) removal was 1.5 g L\(^{-1}\), where the adsorption capacity was 16.91 mg g\(^{-1}\), and the removal percentage was 96.56%, as shown in Fig. 2S (Supplementary File).

Considering that pH determines the dissociation of functional groups and the charge of active sites, studies have shown that pH plays a very important role in determining the adsorption capacity [17] and is one of the main factors affecting the sorption
Fig. 9 Scanning electron micrographs for the chars a C700, b C800, and c C900
Therefore, the pH of the solution is an important parameter to be controlled during the adsorption process. So, experiments were carried out to determine the most appropriate pH. These experiments were conducted in a pH range between 1 and 6, as the hydroxides formed by Cu(II) ions started to precipitate from pH 6 [27, 50]. As shown in Fig. 3S, the Cu(II) adsorption on C700 was extremely pH-dependent. Adsorption capacities ($q$) ranged from 2.06 (pH 1) to 18.45 mg g$^{-1}$ (pH 6). The low adsorption capacity values found until pH 3 can be related to the solution's excess of H$_3$O$^+$ (hydronium ions). At low pH, excess hydronium ions (H$_3$O$^+$) compete with the ions Cu(II) to access the active sites on the adsorbent surface, resulting in blockage for heavy metal adsorption [16, 17, 27]. As the pH increases, this competition lowers, and the adsorption is better. However, the Cu(II) ions precipitate at a pH higher than 5.5 because of the high concentration of OH$^-$ ions in the solution, forming hydroxide forms, so pH 6 could not be performed well [59]. At a high pH, heavy metal ions, like Cu(II), form a precipitate with coexisting ions or in the form of their hydroxides (in this case, forming the hydroxide Cu(OH)$_2$) [53]. Generally, the best performance of an adsorbent is observed in neutral or slightly acidic conditions [17]. Studies mentioned the reduction of sorption capacity at lower pH values [16], which can be noted in Table 3 with the studies of metal adsorption. The results obtained determined pH 5.5 for the other experiments, which corresponds to an adsorption capacity of 18.06 mg g$^{-1}$. This result agrees with that found in the literature [30].

As the pH increases, this competition lowers, and the adsorption is better. However, the Cu(II) ions precipitate at a pH higher than 5.5 because of the high concentration of OH$^-$ ions in the solution, forming hydroxide forms, so pH 6 could not be performed well [59]. At a high pH, heavy metal ions, like Cu(II), form a precipitate with coexisting ions or in the form of their hydroxides (in this case, forming the hydroxide Cu(OH)$_2$) [53]. Generally, the best performance of an adsorbent is observed in neutral or slightly acidic conditions [17]. Studies mentioned the reduction of sorption capacity at lower pH values [16], which can be noted in Table 3 with the studies of metal adsorption. The results obtained determined pH 5.5 for the other experiments, which corresponds to an adsorption capacity of 18.06 mg g$^{-1}$. This result agrees with that found in the literature [30].

Table 3 compares the results obtained in this work with others already published. We evaluated works that used grapes as biomass and their residues to produce adsorbents or other biomasses that adsorbed copper and other ions of metal.

Table 2 Textural properties of chars produced from GB

| Char | Specific surface area (mg$^2$ g$^{-1}$) | Total pore volume (cm$^3$ g$^{-1}$) | Pore diameter (Å) |
|------|---------------------------------------|----------------------------------|------------------|
| C700 | 0.6930                                 | 0.003542                         | 240.6            |
| C800 | 19.0671                                | 0.004439                         | 87.2             |
| C900 | 20.8197                                | 0.006814                         | 69.4             |

Fig. 10 N$_2$ adsorption/desorption isotherms of the chars a C700; b C800; and c C900

Fig. 11 Cu(II) removal percentage and adsorption capacity results (error bars are standard error for 3 replicates)
adsorption process, which is possibly related to Cu(II) adsorption. These bands correspond to the C=C stretching vibration in the char structure [26, 52] and the C-N bonds of amides or amines or C-H bonds [54], respectively. Moreover, there is a small band displacement at 3445.97 cm\(^{-1}\), corresponding to O–H bonds [14, 52, 53] to 3450.79 cm\(^{-1}\) before and after adsorption. These strong shifts in the spectrum after adsorption confirm that the functional groups present on the surface of the adsorbent play an important role in the Cu(II) adsorption, as suggested in Fig. 12.

It is suggested that electrostatic attraction is the main mechanism governing the Cu(II) adsorption onto C700 (see the role of the surface functional groups and the pH-dependent adsorption). The deprotonation of these groups with increasing pH might provide more negatively charged sites, resulting in increased electrostatic attraction [61, 62].

### 3.6 Cu(II) adsorption kinetics

With a dosage of 1.5 g L\(^{-1}\) and a pH of 5.5, kinetic studies were conducted. The initial Cu(II) concentrations varied from 30 to 200 mg L\(^{-1}\). Figure 13a shows the obtained kinetic curves. It is possible to verify that the adsorption process is fast in the first 10 min and, afterward, gradually decreases. For all initial concentrations, equilibrium was reached within 60 min. It can also be seen that the increase in the initial concentration promoted an increase in the adsorption capacity. The kinetic profiles were typical; i.e., the adsorption sites on the C700 surface were progressively occupied by the Cu(II) ions, and then, a constant value of adsorption capacity was reached (equilibrium).

Table 1S (Supplementary Material) presents the kinetic parameters obtained by fitting the experimental kinetic curves with the PFO and PSO models. Through comparisons between the coefficient of determination (\(R^2\)), \(AIC\) (Akaike’s information criterion), and the average relative error (ARE), it can be seen that the PSO model was better fitted to the kinetic data, with this one presenting the highest values of \(R^2\) and lower values of \(ARE\) and \(AIC\) [63]. This fact can indicate the external and internal mechanisms that control the Cu(II) adsorption [47]. In adsorption capacity, the parameter \(q_0\) increased with the initial Cu(II) concentration, from 17.66 to 29.17 mg g\(^{-1}\), and this behavior is close to the experimental. However, the \(k_2\) parameter presented no clear trend regarding the initial concentration in adsorption rate. Besides, overall, the \(h_0\) parameter increased with the Cu(II) concentration. However, the trend is physically consistent since this parameter is related to the initial adsorption stages, where external mass transfer controls adsorption.

### 3.7 Cu(II) adsorption isotherms and thermodynamics

Cu(II) adsorption equilibrium isotherms onto C700 were obtained at four different temperatures (25, 35, 45, and 55 °C). The adsorption isotherms obtained are shown in Fig. 13b. The curves shown are classified as type I isotherms, which indicates the high affinity between Cu(II) and C700 active sites. Figure 13b also shows that the increase in temperature favors the adsorption process. This trend can be explained by the increase in the energy of the Cu(II) ions at higher temperatures. Liu et al. [64] found a similar adsorption profile, studying the Cu(II) adsorption on modified char.

Langmuir [37] and Freundlich’s [36] models were adjusted to the experimental data obtained, and the calculated parameters are shown in Table 2S (Supplementary File). By evaluating the coefficient of determination (\(R^2\)), \(AIC\), and the average relative error (ARE), it can be concluded that the Freundlich model was the best fit for the experimental data. The best fit presented by the Freundlich model suggests that the surface of the C700 adsorbent has heterogeneous active sites [47, 55]. This trend corroborates the FTIR spectra obtained (Fig. 7), which showed that C700 contains different functional groups, like carboxyls, alcohols, amides, and amines. Furthermore, the \(K_f\) parameter increased with the temperature, confirming the better Cu(II) adsorption at 55 °C. Finally, the values found for \(n\) were greater than 1, which means that the Cu(II) adsorption onto C700 was favorable.

The maximum experimental adsorption capacity obtained for Cu(II) was 42 mg g\(^{-1}\) at 55 °C. However, at ambient temperature, the value was 25 mg g\(^{-1}\). Du et al. [65], He et al. [66], and Liu et al. [64] compared around 30 different adsorbents used for Cu(II) uptake from aqueous solutions under different experimental conditions. They found that the adsorption capacities ranged from 0.048 to 175 mg g\(^{-1}\). In this way, we can consider that C700 is a good alternative for Cu(II) trapping from aqueous solutions in terms of adsorption capacity.

The thermodynamic parameters of Gibbs free energy change (\(\Delta G^\circ\)), enthalpy change (\(\Delta H^\circ\)), and entropy change (\(\Delta S^\circ\)) were determined using Freundlich parameters (\(K_f\) and 1/\(n\)) to understand the thermodynamic behavior of the Cu(II) adsorption onto C700. The values of \(\Delta H^\circ\) and \(\Delta S^\circ\) were estimated, respectively, through the values of angular and linear coefficients of the Van’t Hoff graph. The value of the determination coefficient (\(R^2\)) of Van’t Hoff was 0.9902. All the \(\Delta G^\circ\) values were negative and ranged uniformly from −5.22 to −6.59 kJ mol\(^{-1}\) with the temperature increase. So, the Cu(II) adsorption on C700 was spontaneous and favorable [67], and also, it is preferred to use 55 °C. The \(\Delta H^\circ\) value was 8.29 kJ mol\(^{-1}\). The positive \(\Delta H^\circ\) value suggests endothermic behavior, and the magnitude of the \(\Delta H^\circ\) value suggests physical adsorption [24, 67]. The endothermic behavior can be related to the desolvation of water molecules from the char surface, which occurs before the Cu(II) adsorption. The \(\Delta S^\circ\) value was 0.045 kJ mol\(^{-1}\) K\(^{-1}\), indicating that the adsorption process was irreversible and favorable for the sorption stability [67]. Besides that, it can be observed that only...
| Biomass feedstocks | Method of preparation adsorbent | Contaminants | Isotherm | Kinetic model | pH | $q_{MAX}$ (mg g$^{-1}$) | % Removal | Reference |
|-------------------|--------------------------------|--------------|----------|---------------|----|---------------------|-----------|----------|
| Grape bagasse     | Pyrolysis (700, 800, and 900 °C) | Cu(II)       | Freundlich | PSO           | 5.5 | 42.00               | 96.56     | This work |
| Palomino Fino grape seeds | Biosorbent (no treatment) | Cr(VI)       | Freundlich | PSO           | 5.5 | 208.30              | 91.70     |          |
| Grape bagasse     | Pyrolysis (600, 800, and 1000 °C) | Hg(II)       | Langmuir   | PSO           | 4.0 | 45.90               | -         |          |
| Grapefruit peel   | Pyrolysis (450 °C) and modification—hydrogel beads | Cu(II) | Freundlich | PSO           | 6.0 | 80.60               | -         |          |
| Grape bagasse     | Sol–gel method | Basic Blue 41 dye | Langmuir | PSO           | 6.0 | 268.00              | 80.00     | [48]     |
| Grape bagasse     | Potassium hydroxide and carbonization at 799 and 85 °C | Methylene blue | Langmuir | PSO           | 7.0 | 847.00              | -         | [4]      |
| Grape stalk       | (1) In natura; (2) Modified by phosphoric acid; as (3) activated carbon | Caffeine | Sips | -             |     | (1) 2.0; (2) 2.0; (3) 4.0 |    |          |
| Grape bagasse     | Chemical activation using phosphoric acid (400, 500, and 600 °C) | Cu(II)       | Langmuir and Dubinin-Radushkevich | PSO | 5.0 | 43.47              | 99.42     | [50]     |
| Orange peel (biochar) | Pyrolysis (550 °C) | (1) Cu(II); (2) Ni(II) | - | - | 5.0 | (1) 33.56; (2) 34.65; (3) 96.00; (2) 98.00 | [23]     |
| Sweet lemon peel (biochar) | Pyrolysis (550 °C) | (1) Cu(II); (2) Ni(II) | - | - | 5.0 | (1) 30.80; (2) 38.00; (3) 93.00; (2) 95.00 | [23]     |
| Walnut shell      | - | Cu(II)       | Langmuir   | Thomas kinetic model | 5.8 | 29.06              | -         | [26]     |
| Rice husk biochar | Pyrolysis (550 °C) and physicochemical activation—KOH impregnation at 600, 700, and 800 °C | Cu(II)       | Langmuir   | PSO           | 5.0 | 265.00              | -         | [27]     |
| Banana peels      | Pyrolysis (600 °C) | (1) Cu(II); (2) Cd(II); (3) Pb(II) | (1) Langmuir and Redlich-Peterson; (3) Freundlich and Redlich-Peterson | PSO; (3) PSO | 6.0 | (1) 6.0; (2) 8.0; (3) 6.0 | (1) 75.59; (2) 103.22; (3) 241.94 | (1) 46.40; (2) 7.40; (3) 98.20 | [16] |
| Cauliflower leaves | Pyrolysis (600 °C) | (1) Cu(II); (2) Cd(II); (3) Pb(II) | (1) and (3) Redlich-Peterson; (2) Langmuir | (1) Elovich; (2) PSO; (3) PSO | 6.0 | (1) 6.0; (2) 8.0; (3) 6.0 | (1) 56.25; (2) 70.83; (3) 100.69 | (1) 34.20; (2) 6.40; (3) 74.60 | [16] |
the entropy change contributed to obtaining negative $\Delta G^\circ$ values, suggesting an entropy-controlled phenomenon.

### 3.8 Desorption

The results obtained from the adsorption–desorption are shown in Table 4. The adsorption step was carried out with C700 following the conditions previously determined. Desorption tests were carried out by testing hydrochloric (HCl), nitric (HNO₃), and sulfuric (H₂SO₄) acids. Two concentrations were used for acids: 0.2 and 0.5 mol L⁻¹. Through the results presented, it can be seen that the desorption process does not occur satisfactorily. Due to the low desorption percentages, it is concluded that the material cannot be reused.

### 3.9 Perspective of circular economy

The economic feasibility of producing materials (such as the chars of this work—C700, C800, and C900) is determined by studying the costs of production process steps [68]. Therefore, to be possible to implement on a large scale, it must be economically attractive [69]. For that reason, some of the steps of production must be analyzed as follows:

- Feedstock availability: Large quantities are required, as the amount of available biomass directly impacts production costs [68, 70];
- Feedstock collection: A collection of these large amounts of feedstock requires work hours and is relatively labor-intensive. This stage generally costs more than transportation, about 12% of the total cost of the production of char [68];

### Table 4 Desorption using three different acids with two different concentrations

| Eluent     | Adsorption $q$ (mg g⁻¹) | % Removal | % Desorption |
|------------|-------------------------|-----------|--------------|
| HCl (0.2 mol L⁻¹) | 16.44                   | 96.61     | 57.48        |
| HCl (0.5 mol L⁻¹) | 16.04                   | 93.84     | 56.15        |
| HNO₃ (0.2 mol L⁻¹) | 15.75                   | 92.71     | 45.94        |
| HNO₃ (0.5 mol L⁻¹) | 16.23                   | 95.94     | 50.02        |
| H₂SO₄ (0.2 mol L⁻¹) | 16.44                   | 96.72     | 52.90        |
| H₂SO₄ (0.5 mol L⁻¹) | 16.36                   | 95.98     | 52.57        |

![Fig. 12 FTIR of C700 and C700 after Cu(II) adsorption](image1)

![Fig. 13 a Kinetic curves and b isotherm curves for Cu(II) adsorption onto C700](image2)
Feedstock transportation: The transportation, as reported by Homagain et al. [68], represents 9% of the total production cost;

Feedstock storage: Biomass needs to be stored in someplace intermediate before the processing [69];

Feedstock processing (drying and grinding);

Pyrolysis operation: This is the most costly stage among all production stages. According to Homagain et al. [68], this step corresponds to 36% of the system’s total cost. Fixed and variable cost components must be assumed at this step of the process, as the operating costs include feedstock, labor, utilities, maintenance, and overhead [69];

Energy costs: It is necessary to consider the heating cost, consumed heating energy, and local electrical energy price [71];

Application.

According to Homagain et al. [68], the size and scale of the char system production affect the cost and its economic viability. Furthermore, studies about char production costs typically found that char production systems’ potential economic profitability varies depending on the feedstock used [68, 70]. For that reason, this section covers data on the quantities of grapes generated worldwide per year and the quantities of waste generated through their processing.

Data obtained through the OIV were analyzed from 2009 to 2019 to evaluate the production of grapes and wines. The graphic presented in Fig. 14 shows the data obtained from OIV Advanced Search on Database. As can be noticed, the grape production (sum of fresh and table grapes) worldwide only increased in the period presented. In 2009, the production was 67 million tons. In 2019, this number was 84 million tons. This increase corresponds to 19.95%. Therefore, in 2019, Brazil was responsible for 1.445.705 tons of fresh grape production in the year of greatest production.

Figure 14b presents the production of wine in the same period. In 2018, the wine production sector reached the mark of 294 mlL, the highest than in 2013 (292 mlL). In 2009, at the beginning of the evaluated period, the production was 269 mlL. In 2020, world wine production was estimated at 260 mlL [72]. After 2 consecutive years that can be defined as extremely volatile in 2017 and 2018, global wine production in 2020 was the second consecutive year slightly below the average observed in the last years (the first year of the COVID-19 sanitary crisis highlighted asymmetrical aggregate consumption behaviors in different countries in the world) [72]. Nevertheless, according to Zacharof [2], grape wine is one of the most important alcoholic drinks worldwide and is still in constant growth.

The main six vine-growing countries will represent 56% of the world’s vineyard surface area in 2020, and they are, in descending order, Spain, France, China, Italy, Turkey, and the USA [72]. In Italy, France, and Spain, where wine production is more relevant, the annual grape bagasse generation can reach nearly 1200 tonnes per year [3]. In the Serra Gaúcha, a region in Brazil in the state of Rio Grande do Sul with a long winemaking tradition, the quantity of grapes processed in 1 year is in the order of thousands of tons [73].

According to a survey carried out by Embrapa Uva e Vinho and reported by Mello [74], the production of grapes in Brazil in 2018 reached the mark of 1,592,242 tons, with the southern region responsible for 58.91% of this value. Of the total produced in the southern region, 822,689 tons were produced in the state of Rio Grande do Sul. Rio Grande do Sul is responsible for 90% of the total production of wines and grape juices and approximately 85% of national sparkling wines. In 2018, Rio Grande do Sul production of wines, juices, and derivatives was 542.15 million liters [74].

The increase in production leads to an increase in the amount of waste generated during the winemaking process [75]. For example, in 2011, the ten largest processing companies of wine grapes in Rio Grande do Sul produced 12.11 thousand tons of bagasse from wine cultivars and 24.3 thousand tons of bagasse generated from American and hybrid grapes [76]. In 2017, this number increased in Brazil, and 164 million kilograms of bagasse was generated [76]. In Brazil, the main destination of grape pomace is still composting or animal feed. However, with the growth of grape production and processing in Brazil, the volume of bagasse has been increasing, making it crucial to implement technological solutions to use this agro-industrial residue to generate products with greater added value [75].

Viticulture stands out in the world economy, with 80% of grape production destined for the production of wines and derivatives, which results in about 9 million tons of tailings annually [76].

Vinification involves all of the steps carried out during the elaboration of wine from grapes [73]. Winery activities generate huge amounts of seasonal waste, and this problem has been highlighted due to ecological and economic terms [1]. Wine waste can be called a seasonal problem because it occurs in the southern hemisphere from January to April and between August and October [2]. Therefore, it is a seasonal activity, primarily performed during autumn, and 60–70% of the liquid streams generated are obtained 3 months after starting the process [73].

Alcaraz et al. [4] and Dwyer et al. [6] are some of the authors that present the following data: around 25% (in weight) of the grape results in residues during wine production. It has been estimated that for 100 kg of grapes, around 25 kg of residues is generated, described as 70% of grape skins, 12% of stalks, and 18% of seeds [1].

There is a simultaneous growth in environmental awareness and consciousness among many countries, leading to increased development and improved technologies for treating these residues in winemaking regions. The policy
considers the good capacity of those materials to act as valuable resources with a range of value-added uses [5, 6]. According to Beres et al. [3], countries have the proper policy to manage their agricultural waste, control its disposal, and prevent environmental problems. In these countries (as Canada, reported by Dwyer et al. [6], Spain [73]), politics presents the importance of encouraging companies to try other valorization alternatives of the residue. In addition, companies must invest in new technologies to decrease the impact of agro-industrial residues on the environment and establish new processes that will provide additional sources of income [73].

This work shows an efficient alternative for managing and valorizing the huge seasonal waste generated by winery industries. For example, in Brazil, it is estimated that in 2011 alone, 130,000 tons of waste were generated (bagasse and
grape seeds), considering only the 50 largest Brazilian wineries [76]. Accordingly to Tan et al. [13], the conversion of biomass into char is a "win–win" solution for both improving waste management and protecting the environment.

4 Conclusion

Based on a circular economy concept, this work has presented an alternative to waste management in the wine sector. Chars were produced by pyrolysis of grape bagasse and used to adsorb Cu(II), a common element found in fungicides for grapevines (Cu(OH)2). Grape bagasse was composed of cellulose (3.94%), lignin (41.51%), and hemicellulose (12.37%), with volatile matter higher than 70%, being attractive to generate chars. Depending on the temperature, pyrolysis generated a gaseous fraction from 20 to 33%, being H2 the main gas produced. Regardless of the temperature, pyrolysis yielded around 31% of char. The chars prepared at 700, 800, and 900 °C presented different textural characteristics but similar surface chemistry and potential to Cu(II) uptake. So, it was concluded that the char prepared at 700 °C (C700) is better for Cu(II) adsorption purposes.

The Cu(II) adsorption on the char (C700) was favored at a pH of 5.5 with an adsorbent dosage of 1.5 g L−1. In this condition, the removal percentage was higher than 95%. The Cu(II) adsorption kinetics on the C700 char followed the pseudo-second-order model, reaching the equilibrium within 60 min. The Freundlich model was the proper model to represent the equilibrium, and the Cu(II) adsorption was endothermic, spontaneous, and favorable. The maximum adsorption capacity was 42 mg g−1, being a good value compared to the literature.

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Declarations

Ethics approval Not applicable.

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