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# Potential of Sugarcane Biomass-Derived Biochars for the Controlled Release of Sulfentrazone in Soil Solutions

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## Abstract

Sugarcane bagasse-derived biochars, produced at 350 °C (B350) and 600 °C (B600), were evaluated for their capacity to modify the sorption behavior of the herbicide sulfentrazone (SFZ) in Red–Yellow Latosol (RYL) and to serve as carriers for its controlled release. Batch sorption experiments indicated that SFZ exhibits low affinity for soil and undergoes sorption–desorption hysteresis. Adding B350 biochar (up to 0.30%) did not significantly affect the herbicide sorption, whereas B600 enhanced its retention. Sequential desorption assays were conducted by incorporating SFZ either directly into the soil or into the biochars, which were subsequently blended into the soil (at 0.15% *w*/*w*). The SFZ desorbed more rapidly from the soil than from the biochars, suggesting that the pyrogenic material has potential for modulating herbicide release. Phytotoxicity assessments using Sorghum bicolor confirmed that only SFZ incorporated into B350 (at 0.15% *w*/*w*) retained herbicidal efficacy comparable to its direct application in soil. These findings underscore the potential of B350 biochar as a controlled-release carrier for SFZ without compromising its weed control effectiveness.

**Keywords:** sorption; Freundlich isotherms; pesticide retention; controlled release; phytotoxicity; biochar-amended soil

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## 1. Introduction

The application of herbicides to soil can have both positive and negative effects, depending on the type of herbicide, the method of application, and the soil conditions. When used appropriately, herbicides effectively control weeds and enhance crop productivity. However, indiscriminate use of these compounds can lead to soil and water contamination, as well as negatively impacting biodiversity. Therefore, the responsible use of herbicides is essential, along with consideration of alternative strategies to mitigate their environmental impacts. In this context, the use of biochar has emerged as a promising alternative [1]. The interaction between biochar and pesticides has been extensively studied with the goal of

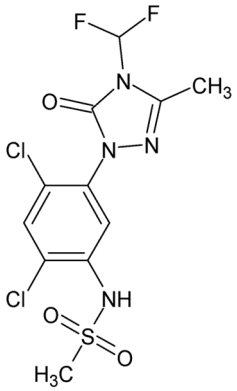
elucidating alterations in the efficiency of active ingredients and assessing the effectiveness of these materials in mitigating environmental contamination caused by these agricultural inputs. The incorporation of pyrogenic materials into the soil modifies the behavior of pesticides in the soil, increasing sorption [1] and persistence [2]. In addition, it reduces the bioavailability [3] and leaching [4] of pesticides from the soil.

The application of biochar as a carrier for the controlled release of pesticides in the soil, particularly herbicides—which constitute the majority of pesticide inputs—can present significant agronomic and environmental benefits. Conventional pesticide application techniques, such as spraying, result in the loss of up to 80% of the applied substances, as they fail to reach the target surface, thereby contaminating the soil and the environment, either directly or indirectly [5,6]. Consequently, there is a pressing need for innovative application technologies, and the use of biochar as a carrier for pesticides could facilitate more targeted application of active ingredients into the soil, preventing the contamination of other environmental compartments.

Recently, several researchers have proposed new slow-release fertilizer formulations utilizing biochar as a carrier [7–9]. Wen et al. [7] demonstrated that the use of cotton stalk biochar as a carrier for ammoniacal nitrogen-based fertilizers effectively reduced the release rate and minimized nitrogen loss through leaching and volatilization at the soil surface. Indeed, the incorporation of biochar improved nutrient efficiency, favoring cotton plant growth compared to the conventional use of $NH_4Cl$. Nonetheless, as is the case for fertilizers, further research is required to evaluate the potential of biochar as a pesticide carrier.

Sulfentrazone (SFZ) {2′,4′-dichloro-5′-(4-difluoromethyl-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl) methanesulfonanilide} (Table 1) stands out among the various pre-emergence herbicides with long residual periods in the soil. This herbicide belongs to the chemical group aryl triazolinone, and its mechanism of action is associated with the inhibition of the enzyme protoporphyrinogen oxidase (PROTOX). It is used worldwide and is recommended for the control of both monocotyledonous and dicotyledonous weeds [10,11]. In Brazil, SFZ is registered for use in crops such as pineapple, coffee, sugarcane, rice, citrus, eucalyptus, tobacco, and soybean [10,11]. The recommended dose of the commercial product varies from 0.6 to 1.6 L/ha, depending on the manufacturer, crop, weed, and environmental conditions [10].

**Table 1.** Physicochemical properties and environmental characteristics of sulfentrazone (SFZ).

| **Sulfentrazone (SFZ)** | **Properties and Characteristics** |
|---|---|
|  | Molecular formula: $C_{11}H_{10}Cl_2F_2N_4O_3S$<br>Molar mass: 387.19 g $mol^{-1}$<br>Vapor pressure at 20 °C: 1.30 × $10^{-4}$ mPa<br>log $K_{ow}$ at 20 °C and pH 7: 0.991<br>Water solubility at 20 °C: 780 mg $L^{-1}$<br>pKa: 6.56 (weak acid)<br>Aerobic half-life: 1.5 years<br><br>$K_{oc}$: 43 ($cm^3$ $g^{-1}$) |

Source: IUPAC [12]; USEPA [13].

Studies conducted under both laboratory and field conditions have shown that SFZ exhibits high water solubility, significant persistence, and mobility through the soil, in

addition to being volatile [12]. Consequently, this herbicide has a high potential for leaching through soil horizons, thus contaminating groundwater, and migrating to surface water [13]. Therefore, herbicide management strategies aimed at ensuring high crop productivity while minimizing environmental impacts are paramount to guarantee sustainable agricultural practices.

The present study investigates the effect of incorporating biochar derived from sugarcane biomass, produced at different pyrolysis temperatures, on the sorption of SFZ in a Red–Yellow Latosol (RYL). Subsequently, SFZ formulations supported on biochar were prepared and subjected to sequential release and biological assays aiming to assess the viability of this technique for the controlled release of the herbicide, thus reducing the environmental risks associated with its usage. The SFZ present in the soil sample extracts used in this study was analyzed by high-performance liquid chromatography (HPLC).

## 2. Material and Methods

### *2.1. Biochar Production*

Sugarcane bagasse was collected from the local market in Viçosa, Minas Gerais, Brazil. It was then dried in a forced-air oven Fanem 320-SE (São Paulo, São Paulo, Brazil) at 60 °C for 48 h to remove moisture (61.4%). The dry biomass was fragmented using a Nogueira DPM-Júnior ensiling machine (Itapira, São Paulo, Brazil) and sieved through 0.425 mm and 0.250 mm mesh sieves. The biomass fraction retained between the two sieves was used for biochar production (0.337 mm average particle size).

The pyrolysis of the sugarcane bagasse was carried out in a F2-DM Fornitec muffle furnace (São Paulo, São Paulo, Brazil). A 100 g sample of the biomass was placed into a cylindrical galvanized steel chamber (radius = 5.5 cm and height = 14 cm), and the remaining empty space was filled with glass wool to prevent biomass combustion. Biochars were produced at 350 °C and 600 °C, with a heating rate of approximately 18 °C $min^{-1}$. Once the desired temperature was reached, the material was held at that temperature for 2.5 h. After the furnace was turned off, the chamber was left inside to cool to room temperature. The biochars produced at 350 °C and 600 °C were designated as B350 and B600, respectively.

### *2.2. Characterization of the Biochars and the Soil*

The elemental composition of the biochars, namely carbon (C), hydrogen (H), nitrogen (N), and oxygen (O) contents, was determined via complete combustion using a TruSpec CHNS/O Micro elemental analyzer (LECO Corp., St. Joseph, MI, USA). The molar ratios H/C and (O+N)/C were calculated to evaluate the aromaticity and polarity of the biochars [14,15]. The distribution of these elements among functional groups was assessed by Fourier transform infrared (FT-IR) spectroscopy, employing a Varian 660-IR spectrophotometer (Mulgrave, Victoria, Australia) equipped with a PIKE GladiATR attenuated total reflectance accessory. Spectral data were collected within the range of 400–4000 $cm^{-1}$.

The specific surface area of the biochars was measured using a Quantachrome Nova 2200e analyzer, based on nitrogen ($N_2$) adsorption isotherms, following the method proposed by Brunauer, Emmett, and Teller [16]. The surface areas were calculated using adsorption isotherm data, over the linear range of 0.01–0.36 $P/P_0$ at –196.15 °C. Prior to analysis, the biochar samples were degassed under vacuum at 180 °C for 24 h [17].

In addition, the biochars were characterized using established methodologies reported in the literature for determining the pH [18,19] and point of zero charge ($pH_{pzc}$) [20–22].

The soil used in this study was classified as a Red–Yellow Latosol (Oxisol). It was collected from the 0–20 cm surface layer at a site with no recent history of herbicide application, located in Viçosa, Minas Gerais, Brazil (20°46′12″ S, 42°52′04″ W). The soil

sample was air-dried and sieved through a 2 mm mesh. Soil characterization was performed at the Laboratory of Soil, Plant Tissue, and Fertilizer Analysis of the Federal University of Viçosa, following the standard procedures established by the Brazilian Agricultural Research Corporation [23].

### 2.3. Chromatographic Analyses

SFZ quantification was performed using a high-performance liquid chromatography (HPLC) system (Shimadzu, Tokyo, Kanto, Japan), which comprised a dual-piston pump (LC-20AT), an autosampler (SIL-10AHT), a column oven (CTO-20A), and a photodiode array detector (SPD-M20A).

The SFZ standard was provided by FMC (Campinas, São Paulo, Brazil), with a purity of 92.01% (*w*/*w*). A stock standard solution (1000 mg $L^{-1}$) of SFZ was prepared by dilution in acetonitrile. The SFZ solutions used for validating the analytical method and the sorption assays were prepared by diluting the stock solution in a 0.01 mol $L^{-1}$ $CaCl_2$ solution.

The chromatographic separation of the analyte from the matrix interferences was achieved using a Shimadzu VP-ODS C18 analytical column (250 × 4.6 mm, 5 µm particle size), thermostated at 30 °C. The elution was carried out under isocratic conditions, with a mobile phase consisting of acetonitrile and deionized water (50:50, *v*/*v*), applied at a constant flow rate of 1.0 mL $min^{-1}$. The injection volume was set at 20 µL, and the SFZ was quantified at a detection wavelength of 207 nm using the external standard calibration method. Calibration curves were established over the concentration range of 0.1 to 12 mg $L^{-1}$, with standard solutions prepared in 0.01 mol $L^{-1}$ $CaCl_2$.

Method validation was conducted according to the guidelines set forth by the Brazilian Health Regulatory Agency (ANVISA) [24] and Directorate-General for Health and Food Safety of the European Commission (DG SANTE) [25]. This process entailed the evaluation of selectivity, linearity, limits of detection (LOD), and quantification (LOQ), accuracy, and intra-day precision. Comprehensive details regarding the validation procedure are provided in the supplementary material (Text S1).

### 2.4. Sorption Kinetics and Batch Sorption–Desorption Experiments in Authentic or Biochar-Amended Soil Samples

These experiments were conducted based on Procedure 106 (Batch Equilibrium Method) of the Organization for Economic Co-operation and Development (OECD) [26].

#### 2.4.1. Kinetic Study

The kinetic study was performed to determine the sorption equilibrium time of SFZ in authentic soil and in soil amended with B350 and B600 biochars. Additionally, the influence of biochar addition on the sorption capacity and sorption rates of SFZ in soil was evaluated. A soil-to-solution ratio of 1:5 (*w*/*v*) was used, and the SFZ solutions were prepared in calcium chloride ($CaCl_2$ 0.01 mol $L^{-1}$) [26]. The soil samples were amended with 0.30% (*w*/*w*) of biochar (B350 or B600) to assess their effects on the sorption kinetic parameters of SFZ in soil. This amendment rate corresponds to an application of 1.50 t $ha^{-1}$ of biochar, assuming incorporation into the upper 5 cm of soil.

In this experiment, 6.00 g of soil sample were suspended in 30.0 mL of $CaCl_2$ solution (0.01 mol $L^{-1}$) containing 10.0 mg $L^{-1}$ of SFZ, using 50 mL polypropylene centrifuge tubes. The suspension was subjected to continuous rotary shaking (70 rpm) for up to 30 h at room temperature (25 ± 2 °C). Following this, the samples were centrifuged at 1700× *g* for 4 min. An aliquot of the supernatant was collected, filtered through a 0.45 µm regenerated cellulose syringe filter, and analyzed by high-performance liquid chromatography (HPLC). All the experiments were performed in duplicate.

The amount of SFZ sorbed was calculated based on a mass balance approach, as described by Equation (1):

$$q_t = (C_0 - C_t) \times \frac{V}{m} \quad (1)$$

where $q_t$ (mg $g^{-1}$) represents the amount of SFZ sorbed at a given time $t$; $C_0$ and $C_t$ (mg $L^{-1}$) denote the initial SFZ concentration and the concentration at time $t$, respectively; $V$ (L) is the volume of the SFZ solution added to the soil or biochar-amended soil samples; and $m$ (g) is the mass of the sample.

The pseudo-first-order, pseudo-second-order, Elovich, and Weber–Morris kinetic models were applied to investigate the sorption behavior of SFZ in both natural and amended soils. The pseudo-first-order model is represented by Equation (2):

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \quad (2)$$

where $q_t$ and $q_e$ represent the amount of SFZ sorbed at a given time $t$ and at equilibrium, respectively, and $k_1$ is the rate constant of the pseudo-first-order model: [27–29].

The pseudo-second-order model is described by Equation (3):

$$q_t = \frac{(k_2 q_e^2)t}{(1 + k_2 q_e t)} \quad (3)$$

where $q_t$ is the amount of adsorbate sorbed at time $t$, $q_e$ is the equilibrium concentration, and $k_2$ is the rate constant of the pseudo-second-order mode [28,30].

The Elovich kinetic model (Equation (4)) is commonly used to describe the chemisorption process [27,31]. However, this model has the limitation of being restricted to the initial stage of the sorption process, as it neglects the occurrence of simultaneous desorption when the sorption process reaches equilibrium [29].

$$q_t = \frac{1}{\beta} ln(1 + \alpha\beta t) \quad (4)$$

where $\alpha$ (mg $g^{-1}$ $min^{-1}$) is the initial sorption rate and $\beta$ (g $mg^{-1}$) is the constant related to the extent of surface coverage and activation energy for chemisorption [28,31]. The value of $1/\beta$ indicates the number of available adsorption sites [31].

The intraparticle diffusion model proposed by Weber–Morris is described by Equation (5):

$$q_t = k_1 t^{1/2} + C \quad (5)$$

where $k_1$ is the intraparticle diffusion rate constant (mg $g^{-1}$ $min^{-0.5}$), $t$ is the time (min), and $C$ is the intercept (mg $g^{-1}$), which may be related to external mass transfer effects [28].

#### 2.4.2. Sorption and Desorption Isotherms

Sorption tests were utilized to investigate the effects of adding B350 and B600 biochars and the percentage of these materials on the sorption behavior of SFZ in the soil.

Sorption isotherms were obtained for soils amended with B350 and B600 biochars, at 0.15% and 0.30%, and for pure soil. Five solutions of the herbicide were used at concentrations of 5, 7.5, 10, 12.5, and 15 mg $L^{-1}$ (prepared by diluting the SFZ standard in a 0.01 mol $L^{-1}$ solution of $CaCl_2$). In a 50 mL propylene tube, 6.00 g of the sample was suspended in 30 mL of the aforementioned solution. The tubes were subjected to agitation for the time taken to achieve the equilibrium previously established. Afterwards, they were centrifuged, and an aliquot of the supernatant was filtered and analyzed by HPLC, similarly to what

was carried out in the experiment to determine the equilibrium time. Three replicates were carried out for each concentration level.

The resulting data were plotted and fitted to the Freundlich model (Equation (6)), which relates the equilibrium concentration of a herbicide in solution ($C_{aq}$, in mg $L^{-1}$) to the amount sorbed into the soil ($C_s$, in mg $kg^{-1}$).

$$C_s^{sor}(eq) = K_f^{sor}\ C_{aq}^{sor}(eq)^{\frac{1}{n}} \quad (6)$$

The Freundlich constant ($K_f^{sor}$, in $mg^{1-1/n}\ L^{1/n}\ g^{-1}$), provided by Equation (6), characterizes the soil's sorptive capacity for a specific compound [32].

Desorption tests were conducted as a continuation of the sorption experiments. All remaining supernatant in the samples from the sorption test was discarded, and then a volume of $CaCl_2$ solution (SFZ-free), equivalent to the volume removed (~24 mL), was added to the sample. The samples were subjected to the same procedures of agitation, centrifugation, and filtration as those used in the equilibrium time determination tests. At the end, filtered aliquots of the supernatant were analyzed by HPLC. Using the obtained data, desorption isotherms were constructed, and the values of $K_f^{des}$ were determined.

### 2.5. Sequential Desorption Assay of SFZ Incorporated into Biochars and Soil

The investigation of the potential application of sugarcane biochar as a carrier for the controlled release of SFZ was conducted through a desorption test with biochars that were incorporated with the herbicide and subsequently added to the soil.

#### 2.5.1. Incorporation of SFZ into the Biochars and Soil

The incorporation of SFZ into the biochars and soil was carried out by fortifying the substrates with solutions of the Boral 500 SC product prepared in acetone. Previously, an emulsion of the commercial product Boral 500 SC was prepared in ultrapure water at a concentration of 10 g $L^{-1}$. This emulsion was then diluted in acetone, due to its good ability to solubilize the emulsion and its rapid volatilization.

The incorporation of SFZ into the biochars was carried out using a 1:1 (mL $g^{-1}$) ratio between the volume of the SFZ solution in acetone and the mass of the biochars. For the soil samples, the ratio was 1:10 (mL $g^{-1}$). These proportions were defined based on the volume required to ensure effective coverage of the particle surfaces of the substrates, without excess solution, and on the apparent density of sugarcane bagasse biochars [33]. The concentration ranges of SFZ incorporated into the biochars and the soil were 16.7–50.0 mg $g^{-1}$ and 0.025–0.075 mg $g^{-1}$ (Table S1), respectively, which corresponds to the same mass range of SFZ used in the sorption tests.

After the herbicide solutions were applied to the substrates, the glass containers (Erlenmeyer flasks) were left open for 72 h to allow solvent evaporation and facilitate the interaction between SFZ and the substrate. The samples were manually shaken three times a day to homogenize the distribution of the herbicide on the surfaces of the substrates.

#### 2.5.2. Consecutive Desorptions

In this assay, soil samples (5.9910 g) were amended with 0.15% (0.0090 g) of B350 and B600 biochars that had been incorporated with different masses of SFZ, resulting in final concentrations ranging from 16.7 to 50.0 mg $g^{-1}$ (Table S1). The release of the herbicide was also evaluated in soil samples (6 g of soil, without biochar) that received direct incorporation of the same SFZ masses applied to the biochars. The concentration range of SFZ in the soil samples was from 0.025 to 0.075 mg $g^{-1}$ (Table S1). The concentration ranges previously mentioned correspond to the same mass range of SFZ used in the sorption isotherm

experiments (Section 2.4.2). A volume of 30 mL of a 0.01 mol $L^{-1}$ $CaCl_2$ solution (free of herbicide) was added to 6.0000 g of sample from each treatment. These samples were subjected to the same agitation, centrifugation, filtration, and chromatographic analysis procedures as the sorption assays described in Section 2.4.1. Three replicates were carried out for each concentration level.

The samples from the previous treatments that received higher masses of SFZ, both the soils amended with fortified biochars and the soil that received direct incorporation of the herbicide were used to assess the consecutive release of the herbicide adsorbed onto the substrates. After each desorption cycle, all excess supernatant was removed (a portion was used for herbicide quantification by HPLC) and replaced with an equivalent volume of $CaCl_2$ solution (free of SFZ).

The percentage of herbicide released into the soil solution during each desorption cycle was determined using Equation (7):

$$\% \, Released = \frac{m_{des}}{m_{in}} \times 100 \quad (7)$$

where $m_{in}$ (mg) and $m_{des}$ (mg) are the masses of SFZ incorporated into the substrates (soil or B350 and B600 biochars) at the beginning of the desorption assay and released (desorbed) into the soil solution during each desorption cycle after equilibrium with the 0.01 mol $L^{-1}$ $CaCl_2$ solution, respectively.

### *2.6. Bioassay*

The agronomic potential of SFZ incorporated into B350 and B600 biochars was investigated through a biological assay conducted in a greenhouse. This assay employed a completely randomized design in a 5 × 7 factorial scheme, with five different substrates (soils amended with SFZ incorporated at 0.15% of B350 and B600 biochars; soils amended with SFZ incorporated at 0.30% of B350 and B600 biochars; pure soil); and seven doses of the herbicide SFZ, which were incorporated onto the biochars or directly into the soil (Table S2). Three replicates were carried out for each concentration level.

The incorporation of the SFZ into the B350 and B600 biochars was carried out similarly to the procedure described in Section 2.5.1, using solutions of the commercial product Boral 500 SC, diluted in acetone. The concentration range of the SFZ in each experiment is presented in Table S2. Unlike Section 2.5.1, in the treatment where the herbicide was incorporated into the soil, the application of the SFZ solution (diluted in acetone) was performed directly onto the experimental unit, 2 h prior to sowing the bioindicator plants, a time sufficient for the evaporation of the solvent.

The experimental units consisted of pots with a capacity of 0.30 $dm^3$, filled with the respective substrates. *Sorghum bicolor* was used as an indicator plant, sensitive to SFZ. Five seeds of the indicator plant were sown in each pot, with each pot considered as an experimental unit. The experiments were conducted in a greenhouse, with the pots being regularly irrigated to maintain the soil moisture near field capacity.

The symptoms of intoxication in the indicator plants caused by the herbicide were evaluated at 7, 14, and 21 days after emergence (DAE) of the sorghum plants. The obtained data were transformed into percentages relative to the controls and used for fitting the non-linear logistic model proposed by Seefeldt et al. [34], according to Equation (8).

$$Y = f(x) = C + \frac{D - C}{1 + \left(\frac{X}{C_{50}}\right)^b} \quad (8)$$

where $C$ and $D$ represent the maximum and minimum levels, respectively, of the dose–response curve; $b$ is the slope of the curve around $C_{50}$; and $C_{50}$ is the dose corresponding to 50% of the response of the variable under study, relative to the response observed in the controls.

### 2.7. Statistical Analyses

All the models used in this study were fitted to the raw data using the Orthogonal Distance Regression algorithm. To compare the parameters generated by the models, a visual inspection of their means and confidence intervals was initially performed. For those parameters with overlapping confidence intervals, the z-test for two independent means was applied.

## 3. Results and Discussion

### 3.1. Characterization of the Biochars and Soil

The gravimetric yields of the B350 and B600 biochars were 27.10% and 23.07%, respectively. The lower yield of the B600 biochar is related to the higher degradation of the major components of the bagasse (cellulose, hemicellulose, and lignin) and the elimination of volatile matter at higher temperatures [35–37].

The B350 and B600 biochars exhibited pH values of 8.26 and 9.63, respectively (Table S3), and points of zero charge ($pH_{pzc}$) of 4.97 and 4.76, respectively (Figure S1 and Table S3). pH values above 7 are associated with the formation of carbonates, hydroxides, and oxides of basic cations ($Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, and $K^{+}$), as well as the loss of acidic functional groups (–COOH and –OH from aromatic compounds) during the pyrolysis process [22,38–40]. The $pH_{pzc}$ values indicated that the surface of the biochars is negatively charged over a broad pH range (pH > 4.80–5.00).

The pyrolysis temperature had a significant effect on the specific surface area of the biochars (Table S3). Higher temperatures led to the formation of biochars with a greater surface area, which may be attributed to the removal of volatile matter up to 475 °C [41] and the development of fine pores in the material at temperatures above 550 °C [42].

The biochar produced at the higher pyrolysis temperature exhibited lower elemental ratios of H/C and (N+O)/C compared to the B350 biochar (Table S3). A lower H/C ratio indicates greater aromaticity, while a higher (O+N)/C ratio suggests increased polarity of the biochars [43]. Therefore, the B600 biochar was more aromatic and less polar than the biochar produced at the lower temperature [14,43,44].

The FTIR spectra of the biochar samples and raw biomass are presented in Figure S2. Compared to the biomass spectrum, the spectra of the biochars showed notable reductions in the intensities of bands associated with –OH stretching (~3400 $cm^{-1}$), attributed to the stretching of hydroxyl groups involved in hydrogen bonding; aliphatic $–CH_2$ stretching (~2900 $cm^{-1}$), related to aliphatic bonds; peaks corresponding to C–O aromatic bond vibrations (1370, 1240, and 1160 $cm^{-1}$; and aliphatic C–O stretching (1090 and 1030 $cm^{-1}$), which are characteristic bands of cellulose, hemicellulose, and lignin [7,36,45].

The formation of new aromatic structures in the biochar produced at 350 °C was observed through the appearance of peaks corresponding to aromatic C=C stretching (at 1580 $cm^{-1}$ and angular deformations of aromatic C–H bonds, attributed to adjacent aromatic hydrogens (between 750 and 870 $cm^{-1}$) [46]. Peaks associated with C=O stretching (at 1705 $cm^{-1}$) confirm the presence of aromatic carboxyl and ketone groups [36].

The disappearance of the bands corresponding to angular deformations of aromatic C–H bonds (between 750 and 870 $cm^{-1}$) in the spectrum of the B600 biochar indicates that hydrogen atoms present in the aromatic rings are eliminated at high temperatures,

as a consequence of the condensation/aromatization process, leading to the formation of polyaromatic structures characteristic of graphene [45].

The characterization of the RYL soil revealed that it is a clayey soil (clay content of 52.8%), acidic (pH 4.96), and contains 3.07% organic matter. Additional soil properties are provided in Table S4.

### *3.2. Kinetic Study*

Kinetic studies were conducted using a 10.0 mg $L^{-1}$ SFZ solution. This concentration of SFZ is 100 times higher than the LOQ. Furthermore, this concentration corresponds to 50 mg $kg^{-1}$ of the active ingredient in the soil, or 100 kg $ha^{-1}$. The results obtained in this experiment, along with the models fitted to the experimental data, are presented in Figure 1. The kinetic parameters and the fitting parameters obtained for each model are shown in Table 2.

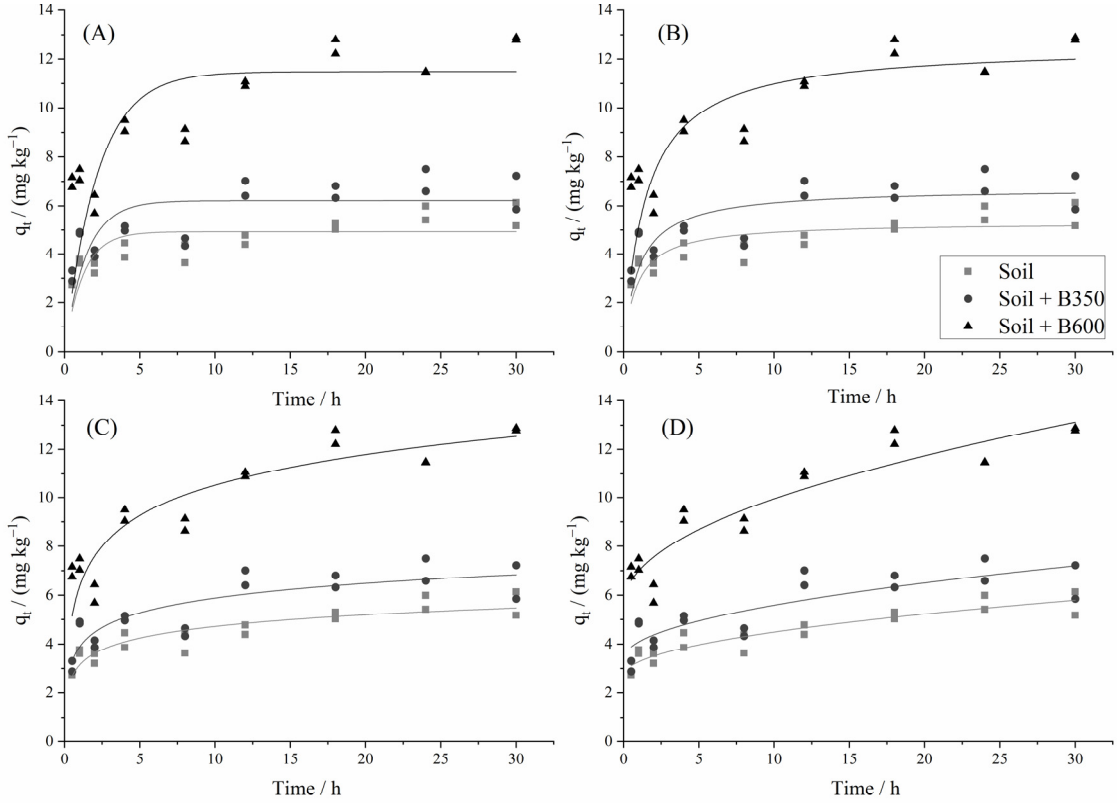



**Figure 1.** Effect of RYL amendment with 0.30% B350 and B600 biochars on the sorption kinetics of SFZ. The sorption kinetics data were fitted using different kinetic models: (**A**) Pseudo-first-order; (**B**) Pseudo-second-order; (**C**) Elovich; and (**D**) Intraparticle diffusion model of Weber–Morris.

All the models provided good fits to the experimental data, with similar fit quality parameters ($R^2$, $s_{res}$).

The pseudo-second-order model showed determination coefficients ($R^2$) greater than 0.99 and low standard deviations of residuals ($s_{res}$), and it stood out, compared to the other models, due to the small errors related to the kinetic parameters generated (Table 2). The curve fitted to the data reveals that the process can be divided into two stages. In the first stage, the SFZ sorption increased rapidly during the first four hours of agitation. In the second stage, the amount of SFZ increased slowly until it reached apparent equilibrium at 16 h. A similar behavior was reported for norfloxacin in different soils [47]. The addition of the biochars, as well as the temperature at which they were pyrolyzed, had significant effects on the amount of SFZ sorbed in the soil ($q_e$).

**Table 2.** Kinetic parameters obtained from the fitting of pseudo-first-order, pseudo-second-order, Elovich, and Weber–Morris models to the sorption kinetics data of SFZ in soil and soils amended with 0.30% (*w*/*w*) of B350 and B600 biochars.

| Kinetic Models | Kinetic Parameters | Treatments | | |
|---|---|---|---|---|
| | | Soil | Soil + B350 | Soil + B600 |
| Pseudo-first-order | $k_1$ ($h^{-1}$) | 0.82 ± 0.22 | 0.70 ± 0.21 | 0.46 ± 0.11 |
| | $q_e$ (mg $g^{-1}$) | 4.93 ± 0.21 | 6.21 ± 0.28 | 11.48 ± 0.41 |
| | $R^2$ | 0.997 | 0.993 | 0.988 |
| | $s_{res}$ (mg $g^{-1}$) | 0.68 | 0.91 | 1.21 |
| Pseudo-second-order | $k_2$ (mg $g^{-1}$ $h^{-1}$) | 0.22 ± 0.07 | 0.15 ± 0.06 | 0.055 ± 0.016 |
| | $q_e$ (mg $g^{-1}$) | 5.32 ± 0.23 | 6.73 ± 0.34 | 12.58 ± 0.49 |
| | $R^2$ | 0.998 | 0.995 | 0.992 |
| | $s_{res}$ (mg $g^{-1}$) | 0.56 | 0.79 | 0.95 |
| Elovich | $\alpha$ (mg $g^{-1}$ $h^{-1}$) | 68.0 ± 51.7 | 76.2 ± 79.9 | 57.4 ± 33.3 |
| | $\beta$ (g $mg^{-1}$) | 1.45 ± 0.19 | 1.15± 0.21 | 0.54 ± 0.07 |
| | $R^2$ | 0.999 | 0.996 | 0.995 |
| | $s_{res}$ (mg $g^{-1}$) | 0.79 | 0.70 | 0.43 |
| Weber-Morris | $k$ (mg $g^{-1}$ $h^{-1/2}$) | 0.56± 0.06 | 0.69 ± 0.16 | 1.37 ± 0.13 |
| | $C$ | 2.72 ± 0.19 | 3.40 ± 0.56 | 5.64 ± 0.46 |
| | $R^2$ | 0.999 | 0.992 | 0.994 |
| | $s_{res}$ (mg $g^{-1}$) | 0.38 | 0.84 | 1.01 |

SFZ is a weak acid (pKa = 6.56) [12] that can exist in its neutral or deprotonated form, depending on the pH of the soil solution. Its molecular structure contains regions of high electron density, such as the aromatic ring and the triazolinone group, which enable electron–donor interactions with neutral sites of low electron density, including metal oxides and surface aluminosilicate groups in the soil. Nitrogen, oxygen, and fluorine atoms present in the SFZ molecule facilitate the formation of hydrogen bonds with hydroxyl groups found in soil organic matter and those bound to aluminum and iron atoms on the surface of soil particles [48].

Biochars possess strongly sorptive aromatic π-systems, which enable π-donor and π-acceptor (hydrophobic) interactions, depending on the substituent groups attached to the aromatic rings of the adsorbates [49]. Accordingly, the addition of biochar to soil facilitates new interactions and enhances the sorption of hydrophobic organic compounds to the substrate [1,50,51]. π–π interactions have also been reported as the primary force driving the interaction between anionic compounds and the surface of pyrogenic materials [52]. Thus, the higher aromatic character of the B600 biochar (as evidenced by its lower H/C ratio) explains its greater contribution to the sorption of SFZ in soil.

The solutions obtained after the sorption experiments exhibited pH values ranging from 5.55 to 5.75, regardless of the type of biochar added to the soil. Under these conditions, approximately 10% of the herbicide molecules are in the deprotonated or anionic form, allowing for electrostatic interactions between SFZ and positively charged sites in the soil, such as aluminosilicates and metal oxides [48].

### *3.3. Sorption/Desorption of SFZ*

To better understand the effects of pyrolysis temperature and biochar percentage on SFZ retention in soil, sorption and desorption isotherms were obtained for RYL soil amended with different percentages of biochars (0.15% and 0.30%) produced at different temperatures (350 and 600 °C). Although sorption equilibrium was observed to be reached within 16 h of agitation, a 24 h agitation period was selected for this experiment.

The sorption and desorption isotherms obtained are presented in Figure 2, along with the curves generated by fitting the Freundlich model to the experimental data. The Freundlich model was fitted using the Orthogonal Distance Regression algorithm, which allows for more accurate estimation of the sorption isotherm parameters [53]. The parameters obtained for each fitted model under each treatment are shown in Table 3.

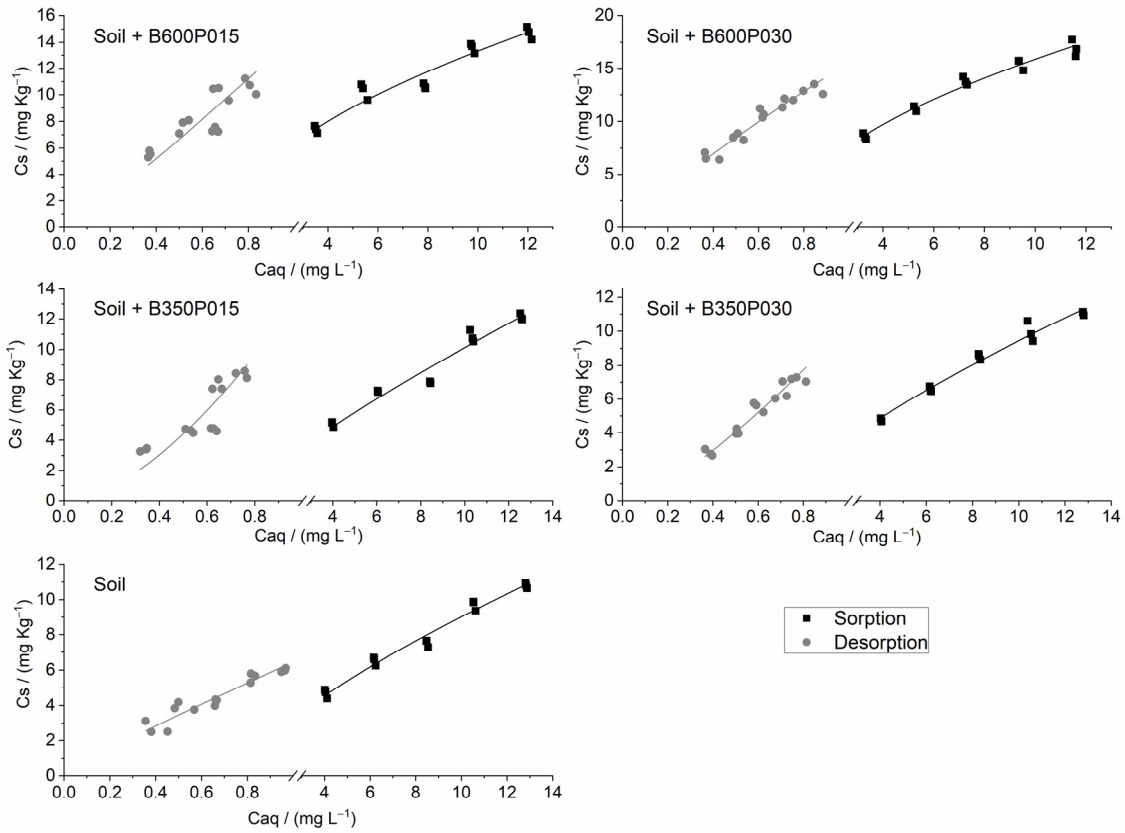



**Figure 2.** Sorption and desorption isotherms of SFZ in unamended soil and in the same soil amended with different percentages (P015: 0.15% and P030: 0.30%) of B350 and B600 biochars.

**Table 3.** Sorption and desorption parameters of SFZ in soil and soil amended with different percentages (0.15 and 0.30%) of biochar obtained at 350 and 600 °C.

| Experiment | Evaluated Phenomenon | Freundlich | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $K_f$ ($\mu g^{1-1/n}(cm^{-3})^{1/n}g^{-1}$) | CI of *Kf* [a] | 1/*n* | CI of 1/*n* | $R^2$ | $s_{res}$ | *H* [b] |
| Soil | Sor [c] | 1.631 ± 0.138 | 1.333–1.929 | 0.742 ± 0.037 | 0.663–0.822 | 0.995 | 0.152 | 1.212 |
| | Des [d] | 6.449 ± 0.216 | 5.982–6.916 | 0.900 ± 0.089 | 0.708–1.092 | 0.999 | 0.071 | |
| Soil + B350P015 | Sor | 1.615 ± 0.210 | 1.161–2.068 | 0.797 ± 0.057 | 0.675–0.920 | 0.988 | 0.191 | 2.088 |
| | Des | 13.977± 2.048 | 9.552–18.402 | 1.665 ± 0.279 | 1.061–2.269 | 0.999 | 0.075 | |
| Soil + B350P030 | Sor | 1.780 ± 0.142 | 1.473–2.087 | 0.725 ± 0.035 | 0.650–0.800 | 0.995 | 0.151 | 1.902 |
| | Des | 10.516 ± 0.554 | 9.318–11.714 | 1.379 ± 0.108 | 1.147–1.611 | 0.999 | 0.053 | |
| Soil + B600P015 | Sor | 3.694 ± 0.407 | 2.815–4.573 | 0.557 ± 0.050 | 0.450–0.664 | 0.987 | 0.213 | 1.995 |
| | Des | 14.388 ± 1.318 | 11.540–17.236 | 1.112 ± 0.192 | 0.697–1.526 | 0.999 | 0.079 | |
| Soil + B600P030 | Sor | 4.605 ± 0.322 | 3.909–5.301 | 0.538 ± 0.032 | 0.468–0.607 | 0.996 | 0.178 | 1.635 |
| | Des | 15.586 ± 0.531 | 14.440–16.732 | 0.879 ± 0.075 | 0.713–1.041 | 0.999 | 0.059 | |

[a] CI of *Kf*: Confidence interval of *Kf* at 95% probability; [b] *H*: Hysteresis coefficient, defined as $1/n_{desorption} = 1/n_{sorption}$; [c] Sor: Sorption; [d] Des: Desorption.

The RYL exhibited a *Kf* value of 1.631 for SFZ sorption, which falls within the same range as reported for other Brazilian and Chinese soils in the literature [1,54]. According to the classification proposed by IBAMA [55], *Kf* values between 0 and 24 are characteristic

of soils with low sorptive capacity for chemical agents. Therefore, the SFZ sorption in the RYL soil is classified as low.

The addition of the B350 biochar to the soil, regardless of the studied percentage, did not result in a significant increase in the SFZ sorption in the soil, which can be confirmed by comparing the confidence intervals (CIs) of the $Kf_{sor}$ values from the Soil+B350P015 and Soil+B350P030 experiments with that of the authentic soil (Supplementary Material, Figure S3). The CI values of the $Kf_{sor}$ from the Soil+B350P015 and Soil+B350P030 experiments considerable overlap the CIs of the $Kf_{sor}$ obtained for the soil, which, according to Cumming [56], generates a large *p*-value (>0.05), indicating that these $Kf_{sor}$ values are statistically identical. The z-test for two independent means was applied to compare the estimated *Kfsor* constants for the unamended soil with those obtained for Soil+B350P015 ($Z = 0.058$, $p = 0.954$) and Soil+B350P030 ($Z = 0.682$, $p = 0.497$). Since $p > 0.05$ in both comparisons, the results indicate that there is no statistically significant difference between the *Kf* values of the unamended soil and those of the Soil+B350P015 and Soil+B350P030 treatments. Therefore, the amendment of soil with up to 1.50 t $ha^{-1}$ of sugarcane biochar obtained at 350 °C does not alter the SFZ sorption *Kf* in the soil.

The modification of the soil with the B600 biochar significantly increased the SFZ retention capacity in the soil, which can be confirmed by the non-overlap of the CI values of the $Kf_{sor}$ from the Soil+B600P015 and Soil+B600P030 experiments with the CI of the $Kf_{sor}$ from the soil (Supplementary Material, Figure S3). When comparing the CI intervals of the $Kf_{sor}$ from the Soil+B600P015 and Soil+B600P030 experiments with each other (Supplementary Material, Figure S3), it is observed that they overlap by more than 50% in both CIs. According to Cumming and Finch [57], in a comparison of two independent means, when the CI overlap (at 95% probability) does not exceed half of the average error margin, the *p*-value is greater than or equal to 0.05. Therefore, since the *p*-value related to the CI overlap of $Kf_{sor}$ is greater than 0.05, it can be concluded that the percentage of biochar (obtained at 600 °C) did not have a significant effect on the SFZ sorption *Kf* in the soil. The comparison of *Kfsor* values between Soil+B600P015 and Soil+B600P030 using the z-test ($Z = 1.593$, $p = 0.111$) confirmed that there is no statistically significant difference between these values.

The higher efficiency of biochars obtained at higher pyrolysis temperatures for improving the sorptive capacity of soil has been previously reported in studies with other organic compounds [43,58]. The greater surface area and the higher aromatic domain of the B600 biochar may be the factors contributing to the higher SFZ sorption in the soil, compared to the B350 biochar [43].

The values of $1/n$ from the isotherms are lower than 1, indicating that the isotherms obtained in this study are non-linear and of type L, which suggests a high affinity (early in the sorption process) between the herbicide and the soil (or soil amended with biochar) [59]. It was also observed that the presence of the B600 biochar in the soil significantly reduced the $1/n$ parameter. The reduction in this parameter has been reported as a consequence of the increase in the aromatic domains of the biochar [14,60], confirming the greater effect of the B600 biochar on $1/n$ (compared to B350 biochar).

The Freundlich desorption coefficients ($Kf_{des}$) obtained are higher than the $Kf_{sor}$, suggesting that the desorption of the SFZ from the soil (and soil amended with biochars) is likely an unfavorable process [61]. Hysteresis (*H*) is a phenomenon that occurs when sorption is nearly irreversible, and the amount of adsorbate returning to the aqueous solution is low. The hypothesis of irreversibility in SFZ sorption is confirmed by the hysteresis coefficients (*H*, Table 3) greater than 1. According to Mamy and Barriuso [62], for no hysteresis to occur in the desorption process, the H value must range between 0.7 and 1. *H*

values close to unity suggest that desorption occurs as soon as the adsorbate is sorbed, and thus the hysteresis phenomenon can be disregarded.

### *3.4. Sequential Release of SFZ in Soil and Biochars*

The potential of biochars as a carrier for SFZ application was investigated through consecutive desorption tests. Desorption tests were conducted with soil samples fortified or soils modified with biochars (B350 and B600) fortified with SFZ. The 0.15% percentage of biochar was chosen as it provides a sufficient content to alter the sorptive capacity (when B600 biochar is used) and because there was no significant difference between the *Kf* values obtained with the addition of 0.15% or 0.30% biochar to the soil (Table 3).

Figure 3 shows the desorption isotherms and curves obtained by fitting the Freundlich model to the experimental data. The parameters obtained for each model are presented in Table 4.

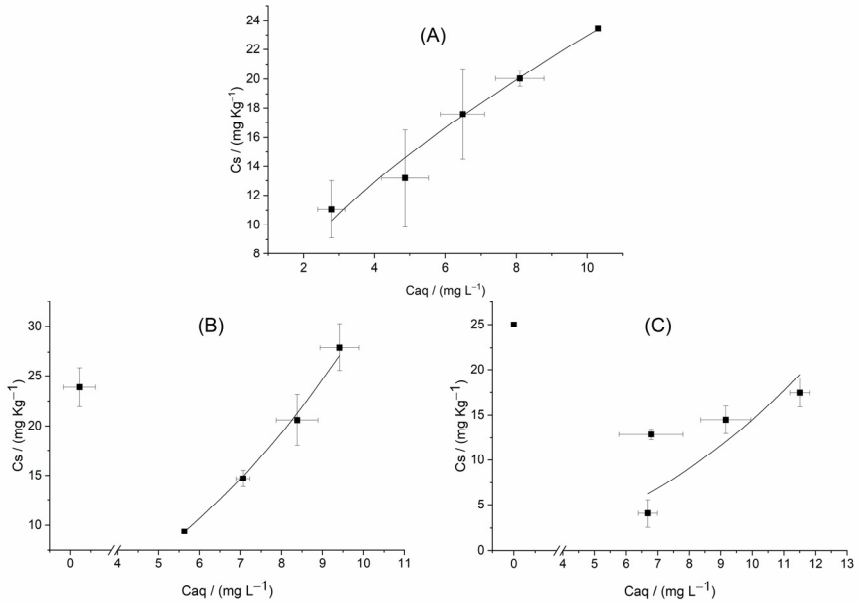



**Figure 3.** Isotherms obtained in the desorption tests of SFZ in soil fortified with the herbicide (**A**) and in soil altered with 0.15% of the B350 (**B**) and B600 (**C**) biochar, both fortified with the herbicide. The isotherms of all treatments received the same initial masses of SFZ. In isotherms B and C, the Freundlich model was fitted to the data starting from the second concentration level, as the SFZ became almost completely immobilized in the substrate (Cs ≅ 25 mg kg$^{-1}$) and was present at very low concentrations in the solution (Caq ≅ 0 mg L$^{-1}$) at the first point of the isotherm.

**Table 4.** Parameters of the SFZ desorption isotherms in soils that received direct incorporation of the herbicide or were altered with 0.15% of B350 and B600 biochars, which were incorporated with SFZ.

| Experiment | Freundlich | | | | | |
|---|---|---|---|---|---|---|
| | $K_f'$ ($\mu g^{1-1/n}(cm^{-3})^{1/n}g^{-1}$) | CI of $K_f'$ [a] | 1/*n* | CI of 1/*n* [b] | $R^2$ | $s_{res}$ |
| Soil-SFZ | 5.403 ± 0.556 | 3.634–7.172 | 0.628 ± 0.047 | 0.479–0.777 | 0.999 | 0.262 |
| Soil + B350-SFZ | 0.262 ± 0.023 | 0.162–0.362 | 2.069 ± 0.050 | 1.852–2.286 | 0.998 | 0.383 |
| Soil + B600-SFZ | 0.117 ± 0.312 | −1.224–1.458 | 2.091 ± 1.135 | −2.787–6.981 | 0.953 | 2.279 |

[a] CI of *Kf*: Confidence interval of *Kf'* at 95% probability; [b] CI of 1/*n*: Confidence interval of 1/*n* at 95% probability.

It can be observed in the isotherms obtained from the experiments with SFZ initially incorporated into the biochar (Figure 3) that the desorptive behavior is completely different from that of the isotherms obtained in the experiments suggested by [26] (Figure 2). In

this study, the soil demonstrated a high capacity for SFZ retention, and the amount of free herbicide in the soil solution was reduced, which can be confirmed by comparing the *Kf'* values (Table 4) and *Kf* values (Table 3). This difference may be related to the fact that in the experiments where the organic sorbate is initially in aqueous solution, there is competition between the sorbate and solvent (water) molecules for the active sites of the sorbent [63]. In the experiment where the SFZ was incorporated into the soil, the contact between the herbicide and the substrate occurs in a dry environment. The solvent (acetone) used to solubilize the commercial product containing the herbicide is largely volatilized, and the interactions between the SFZ and the sorptive sites of the soil become more effective.

The desorption process in the experiments involving SFZ incorporated into biochars can be understood in two distinct stages. In the first stage, which is evidenced at the initial point of the isotherm (initial SFZ mass = 0.15 mg), the interactions between the herbicide and the biochars are sufficiently strong to result in the complete immobilization of the SFZ in the B600 (Figure 3C) and near-complete immobilization in the B350 (Figure 3B). This behavior can be attributed to the strong affinity between the herbicide and the biochars, which hinders its release into the soil solution.

In the second stage, beginning at the second point of the isotherm (incorporation of 0.225–0.45 mg of SFZ into the biochars), the herbicide starts to be gradually released as the initial concentration of SFZ in the biochar increases. This behavior may be associated with the saturation of adsorption sites in the biochars when SFZ masses $\geq$ 0.225 mg are incorporated, causing a significant portion of SFZ molecules to remain on the surface of the material without undergoing effective sorptive interactions. As a result, these molecules are readily solubilized upon contact with the soil solution. This phenomenon is not observed in the fortified soil experiment, in which the initial SFZ was distributed over a soil mass approximately 670 times greater than that of the biochar, thereby providing sufficient sorption sites to interact with the SFZ and enable more effective herbicide retention.

When comparing the curves in Figure 3B,C, obtained after fitting the Freundlich model to the experimental data, with the isotherms from experiments using the same type and percentage of biochar shown in Figure 2, a difference is observed in the sorptive behavior of SFZ in the soil/biochar mixture, depending on whether the herbicide is initially added to the $CaCl_2$ solution or pre-incorporated into the biochar. In the first scenario, the isotherms are classified as type-L ($1/n < 1$, Table 3), indicating a high initial affinity between the SFZ molecules and the sorption sites of the soil/biochar mixture. However, as the herbicide concentration in the soil increases, the intensity of the sorption process decreases due to the increasing difficulty for the herbicide molecules to locate available sorption sites [59,64].

In the second case, the isotherms are classified as type-S ($1/n > 1$, Table 4), which suggests a high competition of the solvent for the adsorption sites [64,65]. This supports the hypothesis of SFZ release from the non-immobilized fraction on the biochar surface, following saturation of the superficial adsorption sites of the biochar (SFZ mass $\geq$ 0.225 mg). Furthermore, this type of isotherm is also indicative of a cooperative sorption process, in which the intermolecular interactions of the SFZ are stronger than the interactions between the herbicide and the aqueous solution, promoting the formation of multiple layers of the herbicide on the adsorbent surface as the herbicide concentration in the soil increases [59,65].

The comparison between the *Kf'* values from the Soil+B350P015 and Soil+B600P015 experiments and the *Kf* values from the experiments with the same percentage and type of biochar (presented in Table 3) is hindered by the significant difference in the $1/n$ values generated in each experimental approach; this is because this parameter affects the units of *Kf* and *Kf'* [26], making the units of these parameters very different. Furthermore, no

significant differences were observed in the $Kf'$ and $1/n$ values for the experiments with the SFZ incorporated into the B350 and B600 biochars.

The sequential release of SFZ was investigated through consecutive desorption assays in fortified soil and soils amended with 0.15% of B350 and B600 biochars fortified with 0.45 mg of SFZ. This experimental approach allowed for a better assessment of the release profile and the reversibility of SFZ sorption on the aforementioned substrates. The cumulative desorption profiles of the SFZ on the substrates are presented in Figure 4.

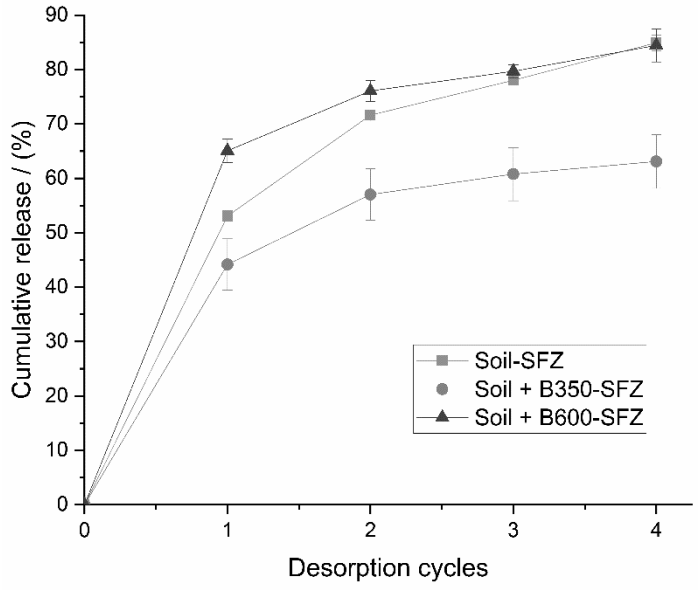



**Figure 4.** Cumulative release of SFZ incorporated into soil and the B350 and B600 biochars (the error bar represents the standard deviation of the triplicates), which were added to the soil at a concentration of 0.15%. The initial SFZ mass in the treatments was 0.45 mg.

As can be observed in Figure 4, the initial desorption of the SFZ in the soil is approximately 50% of the herbicide mass initially incorporated, after which the release of the herbicide is faster than that of the SFZ incorporated into the B350 and B600 biochar. The release profiles of the herbicide in the treatments where the biochar was used as a support indicate a slower release behavior of the active ingredient into the soil solution.

The rapid release of SFZ from the soil may be related to the competition between water molecules for the adsorption sites, where the herbicide is initially sorbed, during soil saturation with the $CaCl_2$ [66].

When the initial incorporation of the SFZ is onto the B350 and B600 biochars, the herbicide molecules, which are sorbed onto the biochars, desorb and gradually diffuse into the soil solution. Throughout the agitation process with the soil, the herbicide molecules released from the biochar may compete for the soil's adsorption sites, thus gradually reducing the total amount of SFZ released into the soil solution [66].

In the treatment where the SFZ was incorporated into the B350 biochar, in addition to exhibiting a slower release of the active ingredient, a lower amount of herbicide was released in the first desorption cycle. This may be associated with a higher number of polar functional groups on the surface of the B350 biochar, which allows for a greater diversity of intermolecular interactions with the SFZ molecules, leading to greater retention of the herbicide under saturation conditions (initial SFZ mass $\geq$ 0.225 mg). On the other hand, the release of the herbicide incorporated into the B600 biochar showed a higher release of SFZ in the first desorption cycle compared to the other treatments. This may be related to a lower diversity of interactions between the herbicide and the biochar. The B600 biochar has lower polarity, allowing predominantly hydrophobic interactions with the herbicide,

which reduces the retention of the herbicide under saturation conditions. Subsequently, the herbicide release rate is lower than that of the fortified soil. Thus, these results demonstrate the potential of these biochars in controlling the release of SFZ in soils.

### *3.5. Assessment of the Agronomic Efficiency of SFZ Incorporated into Biochars Through Bioassays*

The bioassay proved to be effective in assessing the agronomic potential of biochar as a carrier for the application of the herbicide SFZ, as well as in demonstrating the effect of the biochar/SFZ ratio and the type of biochar (the temperature at which it was pyrolyzed) on the herbicide's efficiency. The efficiency of SFZ in the treatments was evaluated based on the symptoms of intoxication (phytotoxicity) caused by the herbicide to the indicator plant at the 14th DAE. Images of the bioassay at 14 DAE are presented in Figure 5.

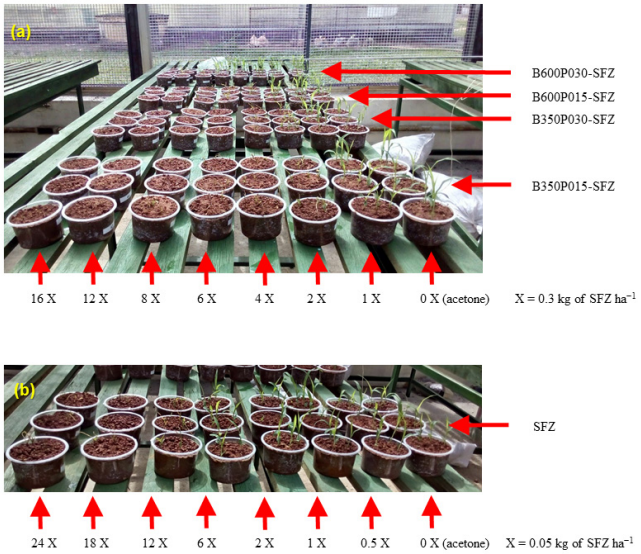



**Figure 5.** Effect of the SFZ application method on the availability of the active ingredient for sorghum plants at 14 DAE. (**a**) Treatments in which SFZ was previously incorporated into different masses of B350 and B600 biochars (0.15% and 0.30% by weight relative to the soil), and (**b**) direct incorporation of SFZ into the soil.

The phytotoxicity curves of the sorghum plants at 14 DAE, as a function of the SFZ doses incorporated into different substrates, are presented in Figure S4. The data were expressed relative to the controls without herbicide application. The equations and the $C_{50}$ values obtained by fitting the model of Seefeldt et al. [34] to the experimental data from the different treatments are presented in Table 5.

**Table 5.** SFZ concentrations required to cause 50% phytotoxicity in plants in treatments with the active ingredient applied directly to the soil or using different masses (0.15% and 0.30% by weight relative to the soil) of B350 and B600 biochars as carriers for SFZ application.

| Treatments | Equation | $C_{50}$ (kg ha$^{-1}$) | CI of $C_{50}$ | $R^2$ |
|---|---|---|---|---|
| Soil-SFZ [a] | $Y = 98.011 + (-0.009 - 98.011)/(1 + (x/0.391)^{3.414})$ | 0.392 ± 0.016 | 0.347–0.435 | 0.999 |
| Soil+B350P015-SFZ [b] | $Y = 100.82 + (3.486 \times 10^{-6} - 100.82)/(1 + (x/0.482)^{2.217})$ | 0.482 ± 0.148 | 0.072–0.893 | 0.999 |
| Soil+B350P030-SFZ [c] | $Y = 99.950 + (9.804 \times 10^{-6} - 99.950)/(1 + (x/0.713)^{3.691})$ | 0.713 ± 0.065 | 0.532–0.894 | 0.999 |
| Soil+B600P015-SFZ [d] | $Y = 100.50 + (0.019 - 100.50)/(1 + (x/1.395)^{4.802})$ | 1.395 ± 0.181 | 0.893–1.897 | 0.999 |
| Soil+B600P030-SFZ [e] | $Y = 93.889 + (-0.028 - 93.889)/(1 + (x/2.547)^{8.400})$ | 2.547 ± 0.171 | 2.072–3.022 | 0.999 |

[a] Soil sample directly fortified with SFZ. [b] Soil with the addition of 0.15% biochar obtained at 350 °C, fortified with SFZ. [c] Soil with the addition of 0.30% biochar obtained at 350 °C, fortified with SFZ. [d] Soil with the addition of 0.15% biochar obtained at 600 °C, fortified with SFZ. [e] Soil with the addition of 0.30% biochar obtained at 600 °C, fortified with SFZ.

The controls of each treatment showed that acetone, the solvent used for preparing the herbicide emulsions, did not cause any phytotoxic effects on the sorghum plants (Figure 5).

As can be observed from the results presented in Table 5, the SFZ dose required to cause 50% intoxication in the indicator plants in the treatment where the herbicide was incorporated into the soil (Soil-SFZ) was 0.392 kg $ha^{-1}$. The incorporation of the herbicide into 0.15% (*w*/*w*) of the B350 biochar did not result in a significant change in the ability of the SFZ to control the indicator plant ($C_{50}$ = 0.482 kg $ha^{-1}$). This can be confirmed by the overlap of the confidence intervals of the $C_{50}$ for this treatment and the Soil-SFZ (Figure S5). The comparison of $C_{50}$ values between the Soil-SFZ and Soil+B350P015-SFZ using the z-test (Z = 0.433, $p$ = 0.666) confirmed that there is no statistically significant difference between these values.

The other treatments showed significant changes in the efficiency of SFZ in controlling sorghum plants, requiring an increase in the amount of active ingredient necessary to cause injury to the plants ($C_{50} \geq$ 0.713 kg $ha^{-1}$). The non-overlap of the confidence interval of the Soil-SFZ treatment with the treatments Soil+B350P030-SFZ, Soil+B600P015-SFZ, and Soil+B600P030-SFZ (Table 5 and Figure S5) confirms this difference [56].

The treatments using the B600 biochar demonstrated the low potential of using this material as a carrier for targeted SFZ application. In these treatments, the amount of active ingredient required to produce toxic effects on the bioindicator plants was even higher than the direct application of the herbicide to the soil or when the B350 biochar was used as a support. This can be explained by the high capacity of the B600 to immobilize the SFZ on its surface at low concentrations ($\leq$16.67 mg $g^{-1}$ Figure 3C), since the concentration ranges of the active ingredient incorporated into the biochars for constructing the dose–response curve were 0.05–0.8 mg $g^{-1}$ and 0.1–1.6 mg $g^{-1}$, respectively, for biochar percentages equivalent to 0.30% and 0.15%.

The increase in the percentage of B600 biochar also contributed to the rise in $C_{50}$ (Table 5), which may be associated with the increase in the number of sorptive sites in a larger mass of biochar, enhancing the herbicide retention capacity [59].

The reduction in the bioavailability of herbicides in soils amended with biochar, as well as the effect of the amendment percentage, has been reported in the literature [1,67,68]. However, it is important to note that in this study, the herbicide was applied to the soil using biochar as a carrier, unlike what is reported in the literature. Liu et al. [1] showed that the addition of rice husk biochar reduced the toxicity of SFZ to *Oryza sativa* plants in different soils. WANG et al. [69] demonstrated that an increase in pyrolysis temperature and the percentage of corn stalk biochar applied to the soil reduced SFZ phytotoxicity to wheat seedlings. Da Silva et al. [67] observed a reduction in the leaching and toxicity of the herbicide clomazone to sorghum plants in soil amended with sugarcane bagasse biochar produced at 400 °C. Nag et al. [68] found lower efficacy of the herbicides atrazine and trifluralin for controlling annual ryegrass in soils amended with up to 1% wheat straw biochar, with this effect being enhanced by an increase in the biochar percentage.

### 3.6. Implications

The results of this study have direct agronomic consequences and environmental implications. B350 biochar can be added to the soil up to a rate of 0.75 t $ha^{-1}$ (up to 0.15%) without altering the availability of SFZ in the soil, and without the need for higher herbicide concentrations to achieve the desired level of weed control, which could result in higher costs for the producer and environmental risk. This biochar, at this proportion (0.15%), also demonstrated the potential to be used as a carrier for the controlled release of SFZ, without compromising herbicide efficiency, which could potentially lead to a reduction in its loss by volatilization and leaching [7].

On the other hand, the use of 0.30% B350 biochar and the application of B600 (at 0.15% or 0.30%) as a carrier for SFZ reduced the herbicide's effectiveness, potentially leading to underdosing (application concentration lower than required) of the active ingredient and resulting in the need for higher doses to control weeds due to the increased sorption of the herbicide by the colloids in the soil/biochar mixture. This adjustment in the doses to be applied could be based on the percentage and type of biochar added to the soil [68], which may result in higher costs for the producer and increased environmental risk.

Nevertheless, the use of this technology may enable the application of this herbicide in soils where its sorption is extremely low, and where low agronomic efficiency and environmental risks of leaching and surface runoff are real concerns.

Further studies should be conducted to evaluate the leaching and persistence of SFZ incorporated into B350 biochar in order to confirm the agronomic and environmental potential of the material, compared to conventional application. The application of this new material in thin surface layers of the soil could concentrate the active ingredient in this layer, preventing it from permeating into deeper soil layers and potentially jeopardizing groundwater reservoirs.

## 4. Conclusions

This study demonstrated the effect of the presence of B350 and B600 biochars on the alteration of SFZ sorptive behavior in an RYL (Oxisol) and the potential use of these biochars as carriers for controlling SFZ release in soil. The addition of up to 0.30% B350 biochar did not alter the SFZ sorption. On the other hand, the addition of only 0.15% B600 biochar was sufficient to increase the herbicide retention in the soil. Desorption tests showed that the sorption–desorption process of SFZ in the soil exhibits hysteretic behavior, and the intensity of this phenomenon is enhanced with soil amendment using the B350 and B600 biochars. Herbicide retention was higher when it was incorporated into the dry substrate. Continuous desorption tests showed that SFZ desorption in the soil is reversible and that the B350 and B600 biochars showed potential as supports to control herbicide release in the soil. Only the B350 biochar, applied at a 0.15% rate, demonstrated agronomic potential to act as a support for SFZ, as it did not alter the amount of active ingredient required to control the indicator plants, compared to the direct application of the herbicide to the soil. Further studies are necessary to better assess the application of biochar in soils with extremely low herbicide sorption, where its use could help mitigate environmental risks.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr13071965/s1, Table S1. SFZ concentrations incorporated into the soil and B350 and B600 biochars in the samples used to obtain the desorption isotherms in tests where the herbicide was applied directly to the soil or on the surface of the biochars. Table S2. SFZ doses in treatments with direct incorporation of the herbicide into the soil or using different percentages (0.15% and 0.30%) of 350 °C and 600 °C biochars as supports for the active ingredient application. Table S3. Properties and elemental composition of the biochars obtained at different temperatures. Table S4. Physicochemical characteristics of RYL. Figure S1. Determination of pHpzc in the biochar samples B350 (a) and B600 (b). Figure S2. FTIR spectrum of the biomass and the biochars obtained at 350 and 600 °C. Figure S3. Freundlich coefficients with their 95% confidence intervals. Figure S4. Dose-response curve of Sorghum bicolor (as a percentage of injury relative to the control) at 14 days after emergence, in substrates that received the incorporation of increasing doses of SFZ, incorporated directly into the soil or previously incorporated into different masses of B350 and B600 biochars (percentages of 0.15% and 0.30%, relative to the soil). Figure S5. C50 of the treatments with SFZ incorporated into the substrates (soil or B350 or B600 biochars) with their 95% confidence intervals. Figure S6. Chromatograms of soil extracts (or soil amended with 0.30% of

B350 and B600 biochars) obtained after 24 h of agitation with 0.01 mol $L^{-1}$ $CaCl_2$ solutions fortified with 15 mg $L^{-1}$ of SFZ or free of the herbicide. Figure S7. Calibration curve obtained by the external standardization method for the determination of SFZ in soil extracts prepared in $CaCl_2$, along with the corresponding residual plot.

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