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Article

Cellulose Acetate Film Containing Bonechar for Removal of Metribuzin from Contaminated Drinking Water

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Abstract: Bonechar presents high sorption capacity for mobile herbicides retained in soil and water. However, its use in a granulated and/or powder form makes it difficult to remove water. The objective of this study was to produce a cellulose acetate film with bonechar as a viable alternative to remove metribuzin from water. The treatments were composed of 2 and 3 g of bonechar fixed on a cellulose acetate film, pure bonechar, and a control (no bonechar). The sorption and desorption study was carried out in the equilibrium batch mode with five concentrations of metribuzin (0.25, 0.33, 0.5, 1, and 2 mg L⁻¹). The water used in the experiment was potable water. Herbicide analysis was performed by High-Performance Liquid Chromatography (HPLC). The addition of 2 and 3 g of the bonechar fixed on the acetate film sorbed 40% and 60%, respectively, of the metribuzin at the lowest concentrations (0.25, 0.33, and 0.5 mg L⁻¹). For both additions, desorption was low, being 7% and 2.5% at 24 and 120 h, respectively. There are still no reports of the production of cellulose acetate film with bonechar for herbicide removal in water, considered an alternative of easy handling and indicated for water treatment plants.

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1. Introduction

Herbicides are initially used to ensure better crop productivity; however, they can lead to the contamination of aquatic ecosystems through retention-related processes (adsorption, absorption, and precipitation), transformation (decomposition or degradation) and transport (drift, volatilization, leaching, and runoff), and by the interactions of these processes [1]. Herbicides applied directly to the soil have the greater potential for groundwater contamination [2]. The mobility of herbicides in soil is coordinated by the movement of water in different directions, being vertical (leaching) and horizontal (runoff and/or running) [3,4]. The physicochemical characteristics of herbicides influence the behavior of the herbicide in the soil and interfere with the final destination of the water. Herbicides with high solubility (S_w) indicate the greater potential for leaching according with the soil water flow. Herbicides that have low S_w also have higher persistence in soil, which reduces groundwater contamination via leaching, but increases surface water contamination by runoff at high rainfall [2,5].

The increasing number of cases of herbicides detection in water is alarming [6]. Atrazine, simazine, diuron, terbuthylazine, ametrine, clomazone, imazapyr, sulfentrazone, and glyphosate have been found in water resources most frequently in Brazil [7–12]. Clomazone, sulfentrazone, diuron, and hexazinone were quantified at concentrations of 56.9, 31.9, 18.8, and 18.8 $\mu\text{g L}^{-1}$, respectively, by means of multiresidue analysis in water samples collected from semi-artesian wells in a rural area of the municipality of Jaboticabal, São Paulo State, Brazil [11]. In water samples collected from 20 farms in the Midwest region of Brazil, including surface water and groundwater, glyphosate herbicide was detected in 3.4% of the samples; however, only two were at levels higher than the limit of quantification (LoQ) of 1.2 $\mu\text{g L}^{-1}$ determined by the chromatographic method [13].

Metribuzin (4-amino-6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one) is classified as a potential contaminant of groundwater and surface water [14] and its maximum residue limit (MRL) in drinking water is $25 \mu\text{g L}^{-1}$ [15]. Metribuzin presents high S_w (10.700 mg L^{-1} at 20°C), high mobility in soil (sorption coefficient normalized by organic carbon content (K_{oc}) from 38 mg L^{-1}), high leaching potential (groundwater ubiquity score (GUS) of 2.96), and low persistence (degradation half-life (DT50)) of ~20 days [16–18]. This is the main herbicide used in vegetables, applied pre-emergence, in systems with exhaustive soil preparation, such as plowing and harrowing, which can favor herbicide losses by leaching and surface runoff. Metribuzin residues were analyzed in water samples from Samambaia River sub-basin at the Federal District and Eastern Goiás State, Brazil [13]. Metribuzin was detected at concentrations above the LoQ of $2.37 \mu\text{g L}^{-1}$ in 73.2% of the water samples.

The use of carbonized organic waste is being evaluated as an alternative for the removal of contaminants from water and soil. Biochar, also called “charcoal”, is a carbon-abundant material from the partial carbonization of plant residues under controlled conditions with no or little oxygen and relatively low temperatures [19]. The main benefits of biochar-based materials lie in their high porosity, specific surface areas, improved ion exchange capacity, and abundant functional groups [20]. Other factors, such as the pH of the biochar (resulting from the pyrolysis condition), the residence time of the biochar in contact with the contaminant, the application rate of the biochar, and the type of contaminant can also affect the sorption of the herbicides [21].

Sorbents of natural origin (e.g., plant biomass) have become attractive due to the availability of abundant inputs, high sorption capacity, and low cost [2]. For example, bonechar (animal-based biochar) is derived from carbonizing animal bones by heating them at $500\text{--}800^\circ\text{C}$ in an airtight iron retort for 4–6 h [22]. Bonechar showed high removal capacity for diuron, ametryn, sulfometuron-methyl, and hexazinone in drinking water [23]. Removal for all herbicides was ~100% at the highest application rate of bonechar (1 g) added to 1 L of water. However, the use of pure bonechar in its granulated and/or powder form makes it difficult to remove it from the water, requiring a centrifugation step to remove the matrix after the herbicide is removed. In addition, the direct application of carbonaceous materials to water can increase the dissolved carbon content, affecting aquatic ecosystems through increased turbidity and metal toxicity [24].

An alternative is the use of a mixed material, in which fine bonechar particles can be added to solid particles by means of biopolymer, which can facilitate the collection and/or reuse of the material after the removal of the herbicide from the water. Cellulose acetate is a natural thermoplastic and biodegradable polymer that is prepared by acetylating cellulose [25]. The way cellulose acetate is processed influences its use, and it can be used for a wide variety of applications, such as for films, membranes, or fibers [26]. Cellulose acetate, being biodegradable, from the natural origin and abundant in the environment, is an environmentally viable alternative to be used as a support material for the doll making. A hybrid film of cellulose acetate with biochar was studied for the sorption ability of phosphorus in water [27]. However, there are still no reports of the production of cellulose acetate films and bonechar for the removal of herbicides in water, being a technological alternative of easy management. Different sorbents have been developed, such as polymer resins [28], particulate carbon [29], nanotubes [30], and mineral materials [31]. Some of these materials have been used to remove herbicides from wastewater, but the high costs limit their use [32].

Thus, the objective of this study was to produce a cellulose acetate film with bonechar as a viable alternative for immobilization and removal of metribuzin from water. The results determine the sorptive capacity of the acetate film and bonechar at different concentrations of metribuzin and that of pure bonechar powder.

2. Materials and Methods

2.1. Drinking Water Samples

The water used was potable and collected from a cold water tap in Viçosa, MG, Brazil, which is regularly used for human consumption. The water for the entire experiment was collected from the tap and stored in a 20 L closed barrel at room temperature. Water samples were used for the determination of the physicochemical properties (Table 1).

Table 1. Selected drinking water quality properties.

Properties	Values
Electrical conductivity ($\mu\text{S cm}^{-1}$)	117.20
Hardness ($\text{mg CaCO}_3 \text{ L}^{-1}$)	22.00
Alkalinity (mg L^{-1})	25.75
Total residual chlorine (mg L^{-1})	1.34
pH	7.25
Turbidity (uT)	0.18
Temperature ($^{\circ}\text{C}$)	16.90
Apparent color (uC)	3.60

Source: Water and Sewage Division of the Federal University of Viçosa, Viçosa, MG, Brazil.

2.2. Bonechar and Cellulose Acetate Film

Bonechar produced from ox bone raw material was purchased from Bonechar Carvão Ativado Ltd.a (Maringá, PR, Brazil) and was used as the sorbent material. The bonechar used had a granulometry of $40 \text{ mm} \times 100 \text{ mm}$. The selected properties of the bonechar are shown in Table 2. The surface morphology was performed by scanning electron microscopy (SEM) on a microscope of the brand JEOL (JSM-6010LA, Akishima, Tokyo, Japan). The resolution was 4 nm (with a beam at 20 kV), the applied magnification was from $8\times$ to $300,000\times$, and the acceleration voltage from 500 V to 20 kV. Biochar particles were attached to a metal surface by a conductive carbon tape (PELCO Tabs™, Ted Pella, Inc., Redding, CA, USA) and coated with gold (Leica EM ACE 600, Buffalo Grove, IL, USA) with a 120-nm-thick layer. The energy-dispersive X-ray spectrometry (EDS) of the doll was characterized by [33,34].

Table 2. Selected properties of the bonechar.

Properties	Values
Feedstock	Cow bone
Production temperature ($^{\circ}\text{C}$)	800
Total surface area ($\text{m}^2 \text{ g}^{-1}$)	200
Carbon surface area ($\text{m}^2 \text{ g}^{-1}$)	50
Carbon content (%)	11
pH (H_2O)	9.12
Soluble ash in acid (%)	<3
Insoluble ash content (%)	0.7
Tricalcium phosphate (%)	70
Calcium sulphate (%)	0.1
Iron (%)	<0.3
Pore size (nm)	7.5–60.000
Pore volume ($\text{cm}^3 \text{ g}^{-1}$)	0.225
Micropore area ($\text{m}^2 \text{ g}^{-1}$)	133
Humidity (%)	<5
Density (g cm^3)	0.65

Source: All information was provided by the manufacturer itself.

The cellulose acetate used had a degree of substitution of 2.5 [35]. To obtain a filmogenic solution, the cellulose acetate was solubilized in acetone (99.8%) at a ratio of 1:10 (w/v) and allowed to stand for 24 h in a completely sealed glass bottle at room temperature.

After this period, cellulose acetate films were produced with bonechar at a proportion of 13.3% (*w/v*) with a thickness of 0.45 mm. For the production of the cellulose acetate film, the filmogen solution with the bonechar was spread evenly over a petri dish with the aid of a glass rod. It was subsequently dried in natural air presenting a good adhesion of the bonechar particles to the film.

2.3. Sorption–Desorption Metribuzin

The methodology for the sorption and desorption study was established according to the OECD guidelines “106, Adsorption—Desorption Using a Batch Equilibrium Method” [36,37]. The stock solution was prepared at a concentration of 500 mg L⁻¹ of the standard Metribuzin-Pestanal™ (analytical standard, 98.8% purity; Sigma-Aldrich, San Luis, MO, USA) and the working solution at a concentration of 100 mg L⁻¹, both in acetonitrile (99.9% purity). Hereafter, five concentrations of metribuzin were prepared (0.25, 0.33, 0.5, 1.0, and 2.0 mg L⁻¹), where the highest concentration corresponded to the highest recommended field dose of the herbicide (1920 g a.i. ha⁻¹) for sugarcane cultivation.

The experiment design was entirely randomized with 3 replicates. The treatments were composed of 2 and 3 g of bonechar fixed on a cellulose acetate film, pure bonechar powder (2 g), and a control (no bonechar added). In a 200 mL Erlenmeyer flask, it was added to 150 mL of drinking water, followed by the concentrations of herbicides and the cellulose acetate film with bonechar. Then, the Erlenmeyer flasks were shaken on a shaking table (Tecnal TE-140; Piracicaba, São Paulo, Brazil) at 100 rpm for 24 h, until equilibrium concentration was reached [38,39]. The pH of the water was measured during the entire sorption and desorption study using a bench pH meter (Digimed, DM-22; Didática, São Paulo, Brazil). Subsequently, three 2 mL aliquots of the supernatant were filtered on a Millipore filter (PRFE membrane 0.45 µm) and placed in vials.

The desorption study was carried out under the same condition as the two-step sorption (24 and 120 h). The water from the sorption study was discarded from the Erlenmeyer flasks containing the films and 150 mL of drinking water, without herbicide, was added again and was stirred on a shaking table for 24 h. Subsequently, three 2 mL aliquots of the supernatant were filtered on a Millipore filter (PRFE membrane size: 0.45 µm) and placed in vials. The amount desorbed was calculated by the difference between the herbicides sorbed on the film and the amount remaining in the supernatant. The same procedure was repeated to analyze desorption at 120 h.

The quantification of metribuzin was performed on a High-Performance Liquid Chromatography (HPLC) system (LC 20AT, Shimadzu, Nagoya, Japan), with a photodiode array detector (SPD-M20A, Shimadzu, Japan) and stainless steel C18 column (Shimadzu VP-ODS Shim-pack 250 mm × 4.6 mm d.i., 5 µm of particle size).

The mobile phase was adapted from [38]. It was composed of acetonitrile/water (acidified with 0.01% phosphoric acid) in a ratio of 45/55 (*v v*⁻¹), an injection volume of 30 µL, a flow rate of 1.0 mL min⁻¹, a wavelength of 254 nm, and a column oven temperature of 30 °C. The mobile phase showed good linearity in the range from 0.05 to 2 mg L⁻¹ of metribuzin. The analytical curve showed a coefficient of determination (*R*²) equal to 0.9992. The limit of detection (LoD) and the limit of quantification (LoQ) were 0.0081 and 0.0289 mg L⁻¹, respectively.

2.4. Freundlich Model for Sorption–Desorption and Apparent Coefficient

The apparent sorption coefficient (*K*_{*d-app*}, L kg⁻¹) was calculated for all concentrations of metribuzin analyzed in the sorption and desorption study, using the following Equation (1):

$$K_{d-app} = C_s / C_e \quad (1)$$

where *C*_{*s*} is the amount of herbicide sorbed onto the bonechar film as Equation (2):

$$C_s = (C_i - C_e) \times V/M \quad (2)$$

where C_i is the initial liquid concentration (mg L^{-1}), C_e is the equilibrium liquid concentration (mg L^{-1}), V is the volume of herbicide solution added (mL), and M is the mass of bonechar (g) [40].

The Freundlich model and its distribution coefficient were determined from Equation (3):

$$K_f = C_s / C_e^{1/n} \quad (3)$$

where n (dimensionless value) can range from 0 to 1, depending on the heterogeneity of the sorption sites.

All isotherms were plotted in Sigma Plot® (version 14.0 for Windows, Systat Software Inc., Point Richmond, CA, USA), and parameter data were presented as means and the standard deviation of the mean ($n = 3$).

3. Results and Discussion

3.1. Synthesis of the Acetate Film with Added Bonechar

The physicochemical properties of the bonechar are presented in Table 2. The material presented a low ash content (0.7%) and a low carbon content (11%), a high tricalcium phosphate content (70%), pH (9.12), and a specific surface area (SSA) ($200 \text{ m}^2 \text{ g}^{-1}$). The surface of the material was irregular, rough and with a varying pore size (Figure 1). A lower surface area was observed for the bonechar produced at different pyrolysis temperatures (350–700 °C) [41]. The authors reported the surface area, the total pore volume, and the average pore diameter of $79.34 \text{ m}^2 \text{ g}^{-1}$, $0.041 \text{ cm}^3 \text{ g}^{-1}$, and 2.09 nm, respectively. Nigri et al. [42] observed a relatively high surface area ($140 \text{ m}^2 \text{ g}^{-1}$) with an irregular pore size and shape.

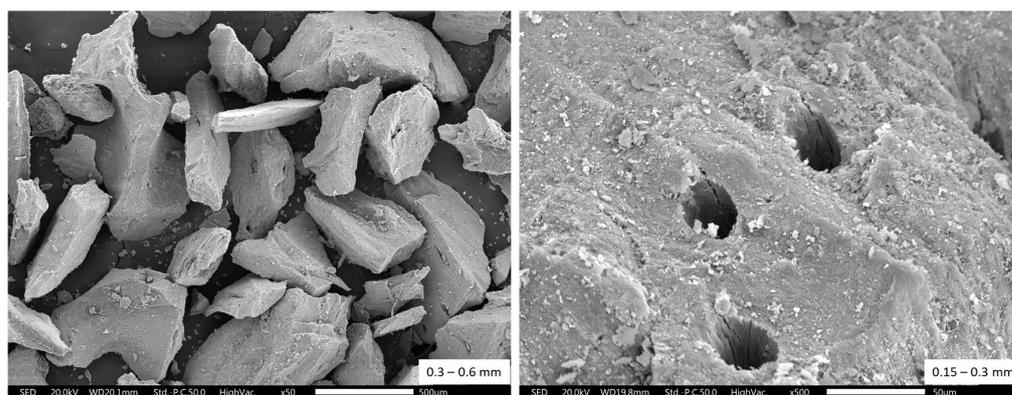


Figure 1. Scanning electron microscopy (SEM) images of the bonechar at two particle sizes: 0.3–0.6 mm and 0.15–0.3 mm at 50× and 500× magnifications, respectively.

The bonechar presents predominance of the elements oxygen (O), phosphorus (P), and calcium (Ca), totaling approximately 80% of the total composition, which is linked to the basic elemental composition of hydroxyapatite [33,41]. Analysis of the elemental composition of the bonechar was performed by energy-dispersive X-ray spectroscopy (EDS) by [33]. The authors reported that C and O appeared as dominant elements (~36% each), with Ca and P also presented mass percentages of ~18% and 9%, respectively. The elements sodium (Na), magnesium (Mg), and chlorine (Cl) were also observed in the bonechar, however, at low concentrations. Bonechar is a material considered highly efficient in removing and immobilizing herbicides [23,33,34,43], as well as fluoride (F) [41], methylene blue [44], chromium (Cr) [45], and arsenic (As) [46] from water and soil. The use of ox bone waste for the production of bonechar not only reduces the risk associated with the waste, but also provides an environmental remediation solution as a potential sorbent for water and soil that can also be used as an alternative organic P [47].

The acetate film with bonechar is seen in Figure 2. The film produced presented good physical structure, with a complete coating of the bonechars granules avoiding

its dispersion in the water. Preliminary studies were necessary to determine the best proportion of the acetate film and the bonechar, since high ratios of the material result in a brittle film and make it difficult to remove from the water. A bonechar-free cellulose acetate film was previously tested for sorption potential of metribuzin and did not show sorptive capacity (unpublished data), so it did not enter into the study for removal of metribuzin from water.



Figure 2. (A) Cellulose acetate film without (pure) and with bonechar; (B) cellulose acetate film with bonechar; (C) visualization of the attachment of the material to the film (translucent water after 24 h of agitation).

3.2. Removal (Sorption/Desorption) of Metribuzin

The addition of 2 g of pure bonechar powder showed a high sorptive capacity (100%) for metribuzin at all concentrations studied, remaining lower than the LoQ (0.0289 mg L^{-1}). The sorption results for 3 g of the bonechar were not presented, since it was not possible to quantify them (Figure 3). In the control treatment (water + metribuzin only), the concentration of the herbicide remained stable throughout the study, excluding the hypothesis of metribuzin degradation. Bonechar is an excellent substitute for activated C due to its higher production and lower activation costs [47]. This material showed the potential for immobilization of different heavy metals in water [42,48–50] and herbicides in soil and water [23,33,34,43]. The bonechar has the high potential in the sorption of metribuzin when used in a powder form; however, it might have complications due to the difficulty in handling the material, such as the removal of the matrix after the removal of the herbicide. Another negative point is the change in the coloration of the water, becoming darker, observed in this study when the pure powdered material was added. For the cellulose acetate film with bonechar, no color change of the water was observed, and the filtration step can be discarded (Figure 2).

Sorption isotherms were fitted using the Freundlich model to describe the sorption of metribuzin on cellulose acetate and bonechar films, as indicated by the coefficients of determination of the equations ($R^2 \geq 0.98$) (Figures 4 and 5). The K_f of sorption was 19.09 and $53.68 \text{ mg}^{(1-1/n)} \text{ L}^{1/n} \text{ Kg}^{-1}$ with additions of film with 2 and 3 g bonechar, respectively. The degree of linearity ($1/n$) varied from 0.43 to 0.89, as the amount of bonechar in the acetate film increased, classifying the sorption isotherm as type L (Table 3). The L-type isotherms indicate that the sorption rate decreases as the herbicide concentration increases [51]. At low concentrations of metribuzin, the material showed higher availability of sorption sites, and at higher concentration, there was a reduction in the potential of the cellulose acetate film with bonechar to sorb metribuzin.

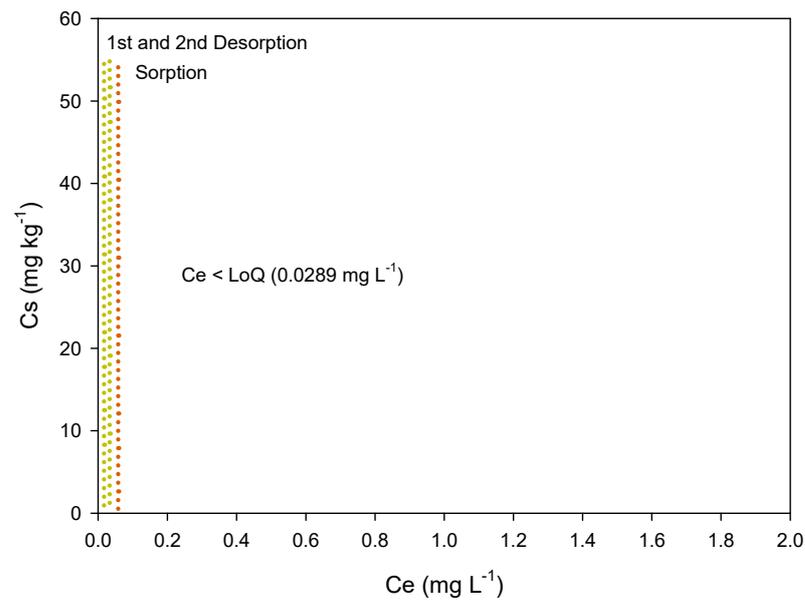


Figure 3. Sorption and desorption isotherms of metribuzin in pure bonechar powder (2 g) added in water. The x-axis indicates the C_e concentration at equilibrium, and the y-axis indicates the C_s concentration in the sorbent. Dotted lines show that no residues of the herbicide were detected (<limit of quantification (LoQ)). One-hundred percent sorption and 0% desorption of the herbicide were observed in the pure bonechar powder.

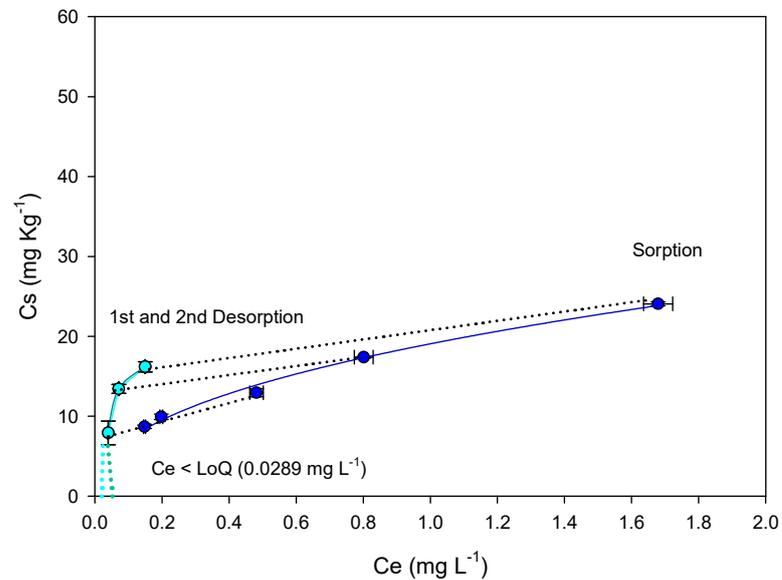


Figure 4. Sorption and desorption isotherms of metribuzin on cellulose acetate film and bonechar (2 g) added to water. The continuous lines in color correspond to the isotherms, and the dotted ones show that no residues of the herbicide were detected (<limit of quantification (LoQ)). The vertical and horizontal bars represent the standard deviation of the means ($n = 3$) of the C_e concentration at equilibrium and the C_s concentration in the sorbent, respectively. Symbols can cover the bars.

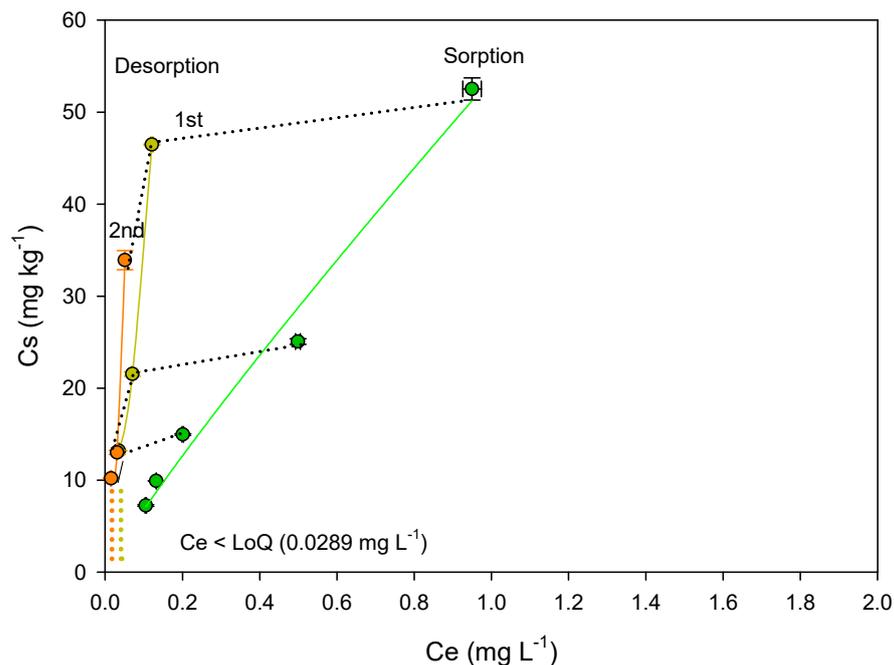


Figure 5. Sorption and desorption isotherms of metribuzin on the cellulose acetate film and the bonechar (3 g) added to water. The continuous lines in color correspond to the isotherms and the dotted ones show that no residues of the herbicide were detected (<limit of quantification (LoQ)). The vertical and horizontal bars represent the standard deviation of the means ($n = 3$) of the C_e concentration at equilibrium and the C_s concentration in the sorbent, respectively. Symbols can cover the bars.

Table 3. Freundlich model isotherm sorption parameters and sorption coefficients (K_{d-app}) of metribuzin on pure bonechar powder and on the cellulose acetate film with bonechar.

Carbonaceous Material	K_f ($\text{mg}^{(1-1/n)} \text{L}^{1/n} \text{kg}^{-1}$)	$1/n$	R^2	Metribuzin (mg L^{-1})				
				0.25	0.33	0.5	1.0	2.0
				K_{d-app} (L kg^{-1})				
Bonechar pure powder (2 g)	<LoQ ^a	-	-	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
(%) sorbed	-	-	-	100	100	100	100	100
Acetate film with bonechar (2 g)	19.06 ± 0.07^b	0.43 ± 0.03	0.995	52.01 ± 0.02	51.21 ± 0.03	58.21 ± 0.03	18.58 ± 0.04	14.33 ± 0.04
(%) sorbed	-	-	-	40.95 ± 0.01	40.08 ± 0.05	43.70 ± 0.02	19.86 ± 0.03	16.04 ± 0.02
Acetate film with bonechar (3 g)	53.68 ± 0.05	0.89 ± 0.02	0.992	78.92 ± 0.03	75.05 ± 0.04	74.43 ± 0.04	50.23 ± 0.01	55.30 ± 0.03
(%) sorbed	-	-	-	67.95 ± 0.01	60.01 ± 0.03	59.81 ± 0.03	50.11 ± 0.02	52.51 ± 0.06

^a Limit of quantification. ^b Mean value of each parameter \pm standard deviation of the mean ($n = 3$). (-) no data available.

The cellulose acetate film with bonechar showed an improvement in the sorption of metribuzin, however compared to that of the pure material, which showed 100% sorption, and the efficiency reduced to ~31% and 57% when adding 2 and 3 g of the bonechar, respectively, which indicates that the use of more films or even a film with a higher concentration of the carbonaceous material can improve the removal efficiency of metribuzin from water. These results were confirmed by the K_{d-app} values of the sorption at the five concentrations of metribuzin shown in Table 3. The acetate film with 2 g bonechar at the lowest concentrations of metribuzin (0.25, 0.33, and 0.5 mg L^{-1}) showed a sorptive capacity of ~40% and a K_{d-app} of ~55 L kg^{-1} . The sorptive capacity decreased to ~16% and the K_{d-app} reduced to ~16 L kg^{-1} , as the concentration of metribuzin increased to 2 mg L^{-1} . However, when 3 g

of bonechar were added, the average K_{d-app} values were ~ 75 and 50 L kg^{-1} for the lowest (0.25, 0.33, and 0.5 mg L^{-1}) and highest (1 and 2 mg L^{-1}) concentrations of metribuzin, respectively (Table 3).

The removal of metribuzin from water with carbonaceous materials was analyzed in different studies [29,52,53]. However, the materials used was in its granular form, which provided greater sorption potential, as observed in this study by the use of bonechar powder. The sorptive capacity of the bonechar is linked to the SSA properties ($200 \text{ m}^2 \text{ g}^{-1}$), C content (11%), and high Ca (18.3%) and P (8.5%) contents [33], which consequently increase the capacity to immobilize potentially toxic compounds [54].

The nature of the carbonaceous material versus herbicide interactions can be exclusively physical, chemical, or both and can result in the phenomenon of sorption. Physical sorption refers to the surface binding process related to the pore size of the carbonaceous material, and chemical sorption refers to binding forces involved, which operate in the formation of compounds [55]. Studies have reported that sorption by bonechar is associated with surface properties (chemical sorption) and carbon content and porosity (physical sorption) [33,34,42,46]. The sorption of metribuzin from aqueous solutions using magnetic and non-magnetic grass biochar was related to hydrogen bonds, Coulomb, van der Waals forces (physical sorption), and π - π interactions (chemical sorption) [56,57].

Bonechar powder had a high pH value (9.12), and it was observed that adding the material to the herbicide-added water increased the pH from 6.8 to an average value of 7.8. By adding bonechar to the cellulose acetate film, regardless of the application rate, the pH increased to 7.3 (Table 4).

Table 4. Changes in pH of the water during the sorption and desorption study of metribuzin in the water with bonechar.

Treatments	Sorption	1st Desorption (24 h)	2nd Desorption (120 h)
Water (with herbicide)	6.91	6.69	6.85
Bonechar pure powder (2 g)	8.72	8.59	7.87
Acetate film with bonechar (2 g)	7.14	7.22	7.39
Acetate film with bonechar (3 g)	7.72	7.25	7.02

Metribuzin is a strong acid (ionization constant, $\text{pK}_a = 1.3$), and its sorption gradually increases as the pH decreases towards the pK_a of metribuzin, which assumes its protonated (negatively charged) form [58]. The bonechar powder, despite changing the pH of the water, showed the ability to sorb 100% of metribuzin, which implicates that the physicochemical characteristics of the material provide high efficiency in the herbicide sorption. The acetate film with bonechar promoted a small pH increase; however, that may have influenced the sorption potential of the film, and further studies analyzing the pH change on the sorptive capacity of the cellulose acetate film with bonechar are needed. Grass biochar and modified (magnetic) grass biochar were analyzed to remove metribuzin from aqueous solutions [57]. These authors observed that low pH values (3–4) of the solution is beneficial for sorption of metribuzin on biochars when compared to high pH values (7) of the solution.

The desorption isotherms were not fitted to the Freundlich model (Figures 4 and 5), since it was not possible to detect the herbicide residues at the lowest concentrations (0.25 and 0.33 mg L^{-1}), as it was lower than the LoQ. Therefore, the model was carried out only from the K_{d-app} of each concentration. The percentage desorbed of metribuzin was $\sim 7\%$ at 24 h (1st desorption) and reduced to $\sim 2.5\%$ at 120 h (2nd desorption) of stirring, regardless of the concentration of bonechar added to the acetate film (Table 5). At 24 h, the K_{d-app} of desorption was $\sim 120 \text{ L kg}^{-1}$ and increased to $\sim 190 \text{ L kg}^{-1}$ at 120 h for the film with 2 g of the bonechar. The film with 3 g of the bonechar showed a desorption K_{d-app} of $\sim 350 \text{ L kg}^{-1}$ at 24 h. On the other hand, at 120 h, the K_{d-app} of desorption varied from 223.2 to 854.4 L kg^{-1} , as the concentration of metribuzin increased from 0.5 to 2 mg L^{-1} (Table 5). The desorption

analyzed for 24 and 120 h at the metribuzin concentrations of 0.25 and 0.33 mg L⁻¹ were less than the LoQ and less than the maximum residue limit (MRL) allowed for metribuzin in water (0.025 mg L⁻¹) [15], which demonstrates its availability for consumption. The highest concentrations of metribuzin (1.0 and 2.0 mg L⁻¹) presented greater desorption than the permitted MRL for both desorption steps. However, the highest dose of the herbicide tested in this study (2 mg L⁻¹) represented the highest commercial dose recommended in the field for metribuzin (1920 g a.i. ha⁻¹), being 80 times higher than the MRL, and possibly only traces of the herbicide could be detected in the water. For the untreated surface and the ground water at Primavera do Leste, Mato Grosso State (Midwestern Brazil), metribuzin was detected at a maximum concentration of 0.00351 mg L⁻¹ [14]. In Portugal, surface waters are collected in river basins, and metribuzin is quantified at a concentration of 0.056 mg L⁻¹ [59].

Table 5. Desorption coefficients (K_{d-app}) of metribuzin on pure bonechar powder and on cellulose acetate film with bonechar at 24 and 120 h.

Carbonaceous Material	Metribuzin (mg L ⁻¹)					Metribuzin (mg L ⁻¹)				
	0.25	0.33	0.5	1.0	2.0	0.25	0.33	0.5	1.0	2.0
	K_{d-app} (L kg ⁻¹)—1st Desorption (24 h)					K_{d-app} (L kg ⁻¹)—2nd Desorption (120 h)				
Bonechar pure powder (2 g)	<LoQ ^a	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
(%) desorbed	0	0	0	0	0	0	0	0	0	0
Acetate film with bonechar (2 g)	<LoQ	<LoQ	113.65 ± 0.01 ^b	111.54 ± 0.04	135.27 ± 0.04	<LoQ	<LoQ	145.85 ± 0.02	194.83 ± 0.01	230.87 ± 0.04
(%) desorbed	0	0	7.50 ± 0.08	7.09 ± 0.05	7.47 ± 0.01	0	0	2.50 ± 0.04	2.93 ± 0.04	2.64 ± 0.07
Acetate film with bonechar (3 g)	<LoQ	<LoQ	373.65 ± 0.04	304.94 ± 0.04	384.40 ± 0.03	<LoQ	<LoQ	223.25 ± 0.06	384.40 ± 0.06	859.47 ± 0.08
(%) desorbed	0	0	6.50 ± 0.07	7.05 ± 0.03	6.04 ± 0.05	0	0	2.20 ± 0.01	3.06 ± 0.04	2.55 ± 0.06

^a Limit of quantification. ^b Mean value of each parameter ± standard deviation of the mean ($n = 3$). (-) no data available.

The films showed sorption potential and low desorption at lower doses of metribuzin, indicating that the greater the active surface area available for sorption of the herbicide, the greater the ability of the sorbent to remove contaminants. Cellulose acetate reduced the available surface area of the bonechar, which reduced the efficiency to ~31% and 57% when adding 2 and 3 g of the bonechar, respectively. A similar result was observed for cellulose acetate used to produce hybrid films with lamellar aluminum magnesium double hydroxides (HDL) as a sorbent for P uptake [60]. HDL incorporated into cellulose acetate had lower phosphate sorption values than HDL powder. The authors reported that a decrease in the sorption potential of the film occurred due to the lower amount of HDLs available for the sorption process.

Cellulose acetate is biodegradable, non-toxic and has the ability to absorb water [61], which makes it potential for use in agriculture, to improve water retention, manufacture of thin films on the surface of various materials. In addition, it has pharmaceutical and biomedical applications as a coating material [62,63]. The biomaterial is biodegradable in soil and can be especially useful in agricultural and horticultural applications [64].

The results are very relevant, when it comes to technologies for removing herbicides from water, presenting high practicality and easy handling. However, despite the film's potential for sorption of metribuzin, its low cost and easy incorporation into cellulose acetate, saturation of the sorptive surface may occur and reduce sorption efficiency when compared to pure bonechar. Strategies should be studied in order to improve the sorption potential of the acetate film with bonechar for higher doses of metribuzin. For example, increasing the amount of the cellulose acetate film with bonechar or successive stages of agitation of the film could contribute to a complete removal of the herbicide from the water. The use of a cellulose acetate film with bonechar for lower doses (0.25, 0.33, and 0.5 mg L⁻¹)

of metribuzin showed a high sorption capacity, and the adoption of the strategies mentioned above can provide complete sorption of metribuzin from water.

4. Conclusions

The use of cellulose acetate for bonechar attachment has not yet been reported in the scientific literature, being a technological innovation for herbicide removal from water. Pure bonechar powder showed a high sorptive capacity for metribuzin at all concentrations tested.

The cellulose acetate film with bonechar presented the higher sorption potential for the lower concentrations of metribuzin in drinking water. The bonechar added at the concentration of 2 and 3 g sorbed 40% and 60%, respectively, of the metribuzin at the concentrations of 0.25, 0.33, and 0.5 mg L⁻¹. For both films, desorption was low, being 7% and 2.5% at 24 and 120 h, respectively.

The film becomes an efficient and easy-to-handle alternative for decontaminating contaminated aquatic environments and can be an alternative for water and sewage treatment plants, as well as for use in spray tanks, washing personal protective equipment (PPE), and household filters.

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