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Cow Bonechar for Pesticide Removal from Drinking Water

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Abstract: Bonechar has been extensively used as an adsorbent. However, using animal bonechar for pesticide removal from water is a method that, to our knowledge, has not yet been reported. This research aimed to evaluate cow bonechar added to contaminated drinking water for removal of five pesticides, hexazinone, diuron, ametryn, sulfometuron-methyl, and azoxystrobin. Drinking water samples were collected from a source that is frequently used for human consumption. Each of the five herbicides was added to the water samples at a concentration of 5 mg mL^{-1}. Cow bonechar treatments to the contaminated water samples (10 mL) consisted in four rates, 0, 0.01, 0.1, and 1 g. High-performance liquid chromatography (HPLC) was used to determine the remaining amount of each pesticide in the water samples, at 1 and 7 d after bonechar treatment. Overall, pesticide removal in the contaminated drinking water samples was in the following decreasing order: azoxystrobin > diuron > ametryn > sulfometuron-methyl > hexazinone. At 7 d after bonechar treatment, no pesticide desorbed this carbonaceous material, remaining strongly retained. For all pesticides, removal close to 100% was achieved with the highest bonechar dose (1 g) added to the water samples. Cow bonechar presents great pesticide removal potential to be used in drinking water contaminated with the pesticides hexazinone, diuron, ametryn, sulfometuron-methyl, and azoxystrobin. Depending on each geographical region, water samples are contaminated with different pesticides. Cow bonechar might be tested more specifically for each region, and could potentially represent a low cost method to be used in water treatment plants or in domestic filters.
Keywords: adsorbent, carbonized biomass, contamination, water remediation

INTRODUCTION

The frequent use of pesticides may lead to the contamination of aquatic ecosystems by direct application, spray drift, aerial spraying, runoff of arable soils or a combination of two or more of the mentioned factors. The pollution of water by pesticides is a topic of considerable environmental interest due to the increasing number of pesticides detected in water [1].

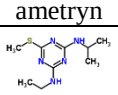
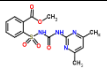
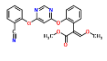
For example, residues of ametryn and hexazinone (0.3 µg L^{-1}) and diuron (8.5 µg L^{-1}) were identified in water samples from natural occurring rivers in Australia [2]. The pesticide monitoring program in South Florida, USA, revealed that ametryn, hexazinone and diuron were the most common pesticides found in surface waters [3]. In Brazil, Armas et al. [4] found levels of 0.3 to 0.5 µg L^{-1} of hexazinone in surface water samples from Corumbataí River and its main effluents. In the same country, residues of diuron and ametryn (0.9 and 0.5 µg L^{-1}, respectively) in rivers from Sergipe State were also detected [5]. Azoxystrobin levels ranging from 0.0008 to 3.03 µg L^{-1} were reported in a recent review about azoxystrobin residues in water [6].

In Brazil, pest management in sugarcane commercial fields is based on chemical control with the use of pesticides. Hexazinone, diuron, ametryn, sulfometuron-methyl, and azoxystrobin are pesticides frequently used in sugarcane pest management programs. The structural formulas of those pesticides, as well as their selected properties are described in Table 1.

Therefore, pesticide adsorption could be a potential pesticide removal method, in view of its efficiency and the ease with which it can be performed in waters containing pollutants. According to Choy and Mckay [8], adsorption is now a widely accepted method in environmental treatment applications worldwide. Liquid-solid adsorption systems rely on the ability of certain solids to preferentially concentrate specific solution substances on their surfaces. This principle, for example, can be used for the removal of pesticides, such as herbicides and fungicides.

Many low-cost sorbents, including agricultural waste and by products, have also been tested in batch and fixed bed adsorption systems [9]. Silva *et al.* [10] showed that banana peel could be used for atrazine and ametryn removal from river and treated waters. On the other hand, biochar (charcoal produced from different feedstock) exhibits a great potential to efficiently tackle water contaminants considering the wide availability of feedstock, low-cost and favorable physical/chemical surface characteristics [11]. Biochar could effectively remove pesticide residues from aquatic environments and thus mitigate pesticide pollution. For example, Taha *et al.* [12] described the adsorption of 15 different pesticides from water using biochar. Herbicide adsorption by biochar was reported for atrazine and simazine [13], 2,4-D, benazolin [14], and diuron [15].

Table-1: **Structural formulas and physico-chemical properties of pesticides**

attribute	hexazinone	diuron	ametryn	sulfometuron-methyl	azoxystrobin
Structural formula					
Pesticide type	herbicide	herbicide	herbicide	herbicide	fungicide
Molecular formula	$C_{12}H_{20}N_4O_2$	$C_9H_{10}Cl_2N_2O$	$C_9H_{17}N_5S$	$C_{15}H_{16}N_4O_5S$	$C_{22}H_{17}N_3O_5$
IUPAC name	3-cyclohexyl-6-dimethylamino-1-methyl-1,3,5-triazine-2,4(1*H*,3*H*)-dione	3-(3,4-dichlorophenyl)-1,1-dimethylurea	*N*2-ethyl-*N*4-isopropyl-6-methylthio-1,3,5-triazine-2,4-diamine	methyl 2-(4,6-dimethylpyrimidin-2-ylcarbamoylsulfamoyl)benzoate	methyl (*E*)-2-{2-[6-(2-cyanophenoxy) pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate
Chemical group - HRAC	triazinone - C1	phenylurea – C2	triazine - C1	sulfonylurea - B	strobilurin
Molecular weight (g mol^{-1})	252.31	233.09	227.12	364.38	403.4
Water solubility at 20°C (mg L^{-1})	33000 (high)	35.6 (low)	200 (moderate)	244 (moderate)	6.7 (low)
Log K_{ow}	1.17	2.87	2.63	-0.51	2.5
pKa at 25°C	2.2 (weak base)	no dissociation	10.07 (weak acid)	5.2 (weak acid)	no dissociation
Vapor pressure at 25°C (mPa)	0.03	1.15×10^{-03}	0.365	7.3×10^{-11}	1.10×10^{-07}
DT50 soil (d)	105	75.5	37	24	78
K_{oc} (L Kg^{-1})	54 (mobile)	813 (slightly mobile)	316 (moderately mobile)	85 (moderately mobile)	589 (slightly mobile)
GUS leaching potential index	4.43 (high leachability)	1.83 (transition state)	0.52 (low leachability)	2.86 (high leachability)	2.65 (transition state)

Source: Adapted from PPDB [7].

Bonechar (biochar of animal origin) capability to adsorb heavy metals, such as lead, cadmium, copper, and zinc, has been recently reported in several natural resources [16,8]. Bonechar is an adsorbent compound constituted of calcium hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$], abbreviated as CaHAP. Bonechar is 76% of CaHAP, which is not only a major inorganic teeth and bones constituent but also phosphate rock [17], containing around 10% carbon and 90% calcium phosphate. Bonechar is mainly produced by the carbonization of bones. This adsorbent compound is derived from the carbonization of crushed animal bones by heating them to 500-800ºC in an airtight iron retort

for 4-6 h [18]. After the heating process, the crushed bones will form the bone charcoal.

Bonechar has been used extensively as an adsorbent for the decolorization of sugarcane [19]. This adsorbent was used as a defluoridating agent [20] and as the adsorbent compound of cadmium in a wastewater treatment system in China [17]. Bonechar was also used for removing arsenic ion from aqueous solution [18]. However, bonechar as an adsorbent to remove pesticides in water has not been reported so far. Therefore, this current work aimed to evaluate cow bonechar added as an adsorbent for removing the pesticides hexazinone, diuron, ametryn, sulfometuron-methyl, and azoxystrobin from contaminated drinking water.

MATERIALS AND METHODS

Drinking Water Samples

Drinking water samples were collected from a cold water faucet in Piracicaba, SP, Brazil, which is regularly used for human consumption. The faucet was opened so that a 1L-bottle was filled at the same flow rate as consumers find to fill up a glass of water. The bottle was stored at room temperature. Samples from the water bottle were used to determine some physico-chemical properties of the collected water (Table 2).

Table-2: **Selected properties of drinking water quality**

property	value	permitted value[a]
chlorine (mg L^{-1})	2.5	<5.0
iron (mg L^{-1})	0.05	<0.3
fluoride ion (mg L^{-1})	0.69	<1.5
manganese (mg L^{-1})	0.02	<0.1
pH	8.3	6.0-9.5
turbidity (NTU)	0.68	<5
color (PCU)	3	<15
fecal coliforms	absent	absent

NTU: nephelometric turbidity units, PCU: platinum cobalt units.
[a]Source: SEMAE [21]

Pesticides

Stock solutions of hexazinone, diuron, ametryn, sulfometuron-methyl, and azoxystrobin were prepared from their respective analytical standards, with 99.9, 99.6, 99.0, 99.5, and 99.5% purity, respectively (Sigma Aldrich, St. Louis, MO, USA; Chem Service, West Chester, PA, USA). All stock solutions were prepared at a concentration of 1,000 μg mL^{-1} in acetonitrile. Working solutions at a 5 mg mL^{-1} concentration was prepared for all pesticides from their respective stock solutions. 50 μL for each working solution was added in the 10 mL of contaminated drinking water samples. Despite being an application rate not often found in drinking water, this rate was used to elucidate the impact of bonechar on removal of pesticides.

Bonechar

Bonechar produced from cow bone feedstock was purchased from Bonechar Carvão Ativado Ltda (Maringá, PR, Brazil) and was used as the adsorbent compound in the drinking water contaminated with the mentioned pesticides. Bonechar was first milled and homogenized in mechanical mill with a mesh of 0.6x0.3 mm, and was further added to the 10 mL water samples in 4 rates, 0 (control), 0.01, 0.1, and 1 g, corresponding to concentration of 0, 1, 10, and 100 g L^{-1}, respectively. The selected properties of the bonechar used in this study are shown in Table 3.

Table-3: **Selected properties of bonechar**

property	value
feedstock	cow bone
production temperature (^oC)	800
total surface area (m^2 g^{-1})	200
carbon surface area (m^2 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 carbonate (%)	7
calcium sulphate (%)	0.1
iron (%)	<0.3
pore size (nm)	7.5 - 60,000
pore volume (cm^3 g^{-1})	0.225
humidity (%)	<5
density (g cm^{-3})	0.65
hardness	>80
aspect	powdered solid
odor	odorless

Source: All information was provided by the manufacturer

Experimental Design

The experiment was completely randomized under a factorial arrangement, with 3 factors varying in different levels: pesticides (hexazinone, diuron, ametryn, sulfometuron-methyl, and azoxystrobin),

bonechar amounts (0, 0.01, 0.1, and 1 g), and days after bonechar application (DAA) (1 and 7 DAA). Each experimental unit consisted of a 50 mL Teflon tube with a screw cap, containing 10 mL of the contaminated drinking water. Three replications were considered.

Pesticides Removal

Batch adsorption experiments were carried out in room temperature (20 ± 2°C) with the shaker set at 200 rpm. After the tubes were shaken for 24 h to reach equilibrium (data not shown), the samples were centrifuged at 4000 rpm for 10 min at 4°C, and supernatants were analyzed at 1 and 7 d after application. Analyzes consisted in determining the concentration of each pesticide present in each sample after the shaking and centrifugation steps in each evaluation time for all treatment combinations. Results are expressed in mg of pesticide per mL of drinking water.

Chromatographic Analysis

The chromatographic method by Mendes *et al*. [22] with some modifications was validated and met the requirements of the Brazilian national guidelines [23] and the European Union [24].

The chromatographic determinations of the initial and final pesticide concentrations of the samples were performed using a high-performance liquid chromatography equipment (HPLC; Agilent Technologies® model 1200 series), possessing an UV-Vis detector (Agilent Technologies®) and a C18 stainless steel column (3.5 x 4.6 x 150 mm d.i., Kromasi). The chromatographic conditions for analyses were: water (with orthophosphoric acid added for pH correction to 2.2) and acetonitrile (40:60, v v^{-1}) as the mobile phase at a flow rate of 1.5 mL min^{-1}, and injection volume of 20 µL. Analyses were performed with a column temperature of 35ºC and wavelengths of 235 and 242 nm. All samples were analyzed in triplicates, and the Chemstation® software was used for data analysis.

Statistical Analysis

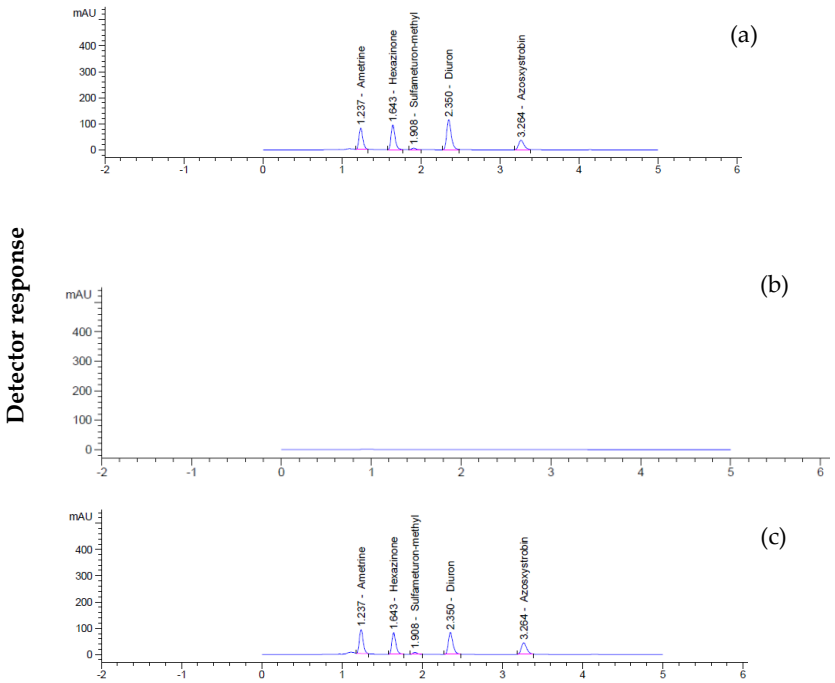
After confirming normality of the data by the Shapiro-Wilk normality test (p<0.05), data were subjected to analysis of variance (ANOVA). Means were compared by the Dunnett's honest significant difference (HSD) test (p<0.05), and figures were plotted using Sigma Plot® (version 10.0 for Windows, Systat Software Inc., Point Richmond, CA, USA).

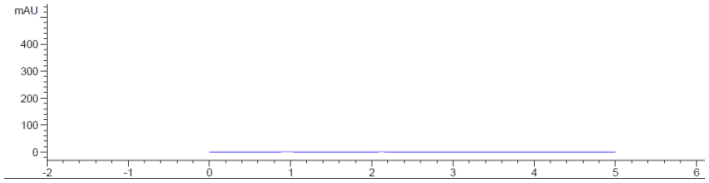
RESULTS AND DISCUSSION

Validation of Chromatographic Method

In order to verify drinking water quality, initial analyzes were performed and no residues of hexazinone, diuron, ametryn, sulfometuron-methyl, or azoxystrobin were detected (Figures 1b and 1d). In Brazil, only diuron has an established maximum environmental concentration in drinking water (90 µg L^{-1}). The maximum environmental concentrations in drinking water for hexazinone, ametryn, sulfometuron-methyl, and azoxystrobin have not been determined in Brazil [25].

By using the peak areas from chromatograms and the concentrations of the standard solutions of each pesticide, the following parameters were determined: selectivity, linearity, limit of detection (LOD), quantification (LOQ), and accuracy of the method (Figure 1). These parameters estimate the reliability of the analytical method [23,24].





(d)

Figure-1: **Chromatogram of hexazinone, diuron, ametryn, sulfometuron-methyl, and azoxystrobin obtained by HPLC at a concentration of 5.0 µg mL^{-1} (a and c) and 0.0 µg mL^{-1} (b and d) in in drinking water with wavelength of 242 (a and b) and 235 nm (c and d). The retention times of ametryn, hexazinone, sulfometuron-methyl, diuron and azoxystrobin were 1.237, 1.643, 1.906, 2.350, and 3.264 min, respectively.**

Identification of each pesticide present in the samples was achieved by comparing the retention times of the respective analytical standard. Pesticide quantification was performed by comparing the peak areas in the chromatograms between the identified pesticides with their respective analytical standards.

The linearity of the HPLC instrument was determined for concentrations of 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 µg mL^{-1} and a calibration curves were determined: y=69.39x+0.76, 96.28x+1.28, 65.72x+0.70, 5.96x+0.006, 41.39x+0.19, for hexazinone, diuron, ametryn, sulfometuron-methyl, and azoxystrobin, respectively, with a correlation coefficient (R^2) of 0.99 for all pesticides.

Parameters LOD and LOQ were measured based on signal to noise ratio, with values ranging from 0.01 to 0.04 and 0.05 to 0.10 µg mL^{-1}, respectably, for all pesticides (Table 4). LOQ and LOD were determined by the analysis of samples with known concentrations of analyte and by establishing the minimum level at which the analyte can be reliably detected and can be quantified with acceptable accuracy and precision, respectably.

Table-4: **Limits of detection (LoD) and quantification (LoQ) of the proposed method for the pesticides in drinking water samples**

pesticide	LOD (µg mL^{-1})	LOQ (µg mL^{-1})
ametryn	0.01	0.05
hexazinone	0.04	0.10
sulfometuron-methyl	0.04	0.10
diuron	0.04	0.10
azoxystrobin	0.04	0.10

Recoveries (%R) for all pesticides ranged between 92.20% and 110.93%, and coefficients of variation (CV) were below 2% (Table 5). According to ANVISA [23] and SANTE [24], acceptable pesticide %R values should range between 70 and 120%, and below 20% for CV values.

Table-5: **Recovery levels (3 injections of each replicate) of the proposed method for the pesticides (5.0 µg ml^{-1}) in drinking water samples**

pesticide	sample								
	1st			2nd			3rd		
	R(%)	±SD	CV(%)	R(%)	±SD	CV(%)	R(%)	±SD	CV(%)
ametryn	92.20	0.10	2.07	92.80	0.01	0.22	94.80	0.06	0.27
hexazinone	97.69	0.01	0.10	99.07	0.01	0.12	99.40	0.00	0.00
sulfometuron-methyl	97.73	0.04	0.77	99.40	0.02	0.35	99.53	0.01	0.12
diuron	96.87	0.01	0.12	97.87	0.01	0.12	98.80	0.00	0.00
azoxystrobin	100.93	0.04	0.70	99.53	0.01	0.23	99.53	0.04	0.71

R(%): recovery percentage, SD: standard deviation, CV: coefficient of variation.

Characterization of the Cow Bonechar

As shown in Table 3, the pH value for the cow bonechar was high (9.12) and insoluble ash content was low (0.7%), produced temperature of 800ºC. Nigri *et al.* [26] characterized a bonechar produced by same company of bonechar studied in this research and analyzed the scanning electron microscope (SEM) images. The authors observed that cow bonechar has a fractured and porous surface, with very irregular shape and varying pore sizes. By using energy dispersive X-ray spectroscopy (EDS) microanalysis, bonechar carbon content, according to the same study, was 12.92% of the total composition. These results are in agreement with our current study, in which bonechar pore size ranged

from 7.5 to 60,000 nm and carbon content was approximately 11% (Table 3). In addition, we determined that the bonechar surface area and pore volume were 200 m^2 g^{-1} and 0.225 cm^3 g^{-1}, respectively. Even presenting a low surface area, the value found in our current study corroborates with the value found by Nigri *et al*. [26]. The characterization of the bonechar is very important to understand the retention process of pesticides in contaminated drinking water.

Quantification of Pesticides in the Drinking Water Samples

No interaction was detected among pesticide, bonechar amount, and evaluation time on pesticide residues in the drinking water studied ($P > 0.05$). However, a significant interaction between pesticide and bonechar amount was detected ($P < 0.01$). At 1 and 7 d after bonechar application, pesticide residues were detected at the same concentration in the water samples for any of the pesticides, indicating that those were likely strongly adsorbed by bonechar and the desorption process did not occur (Figure 2).

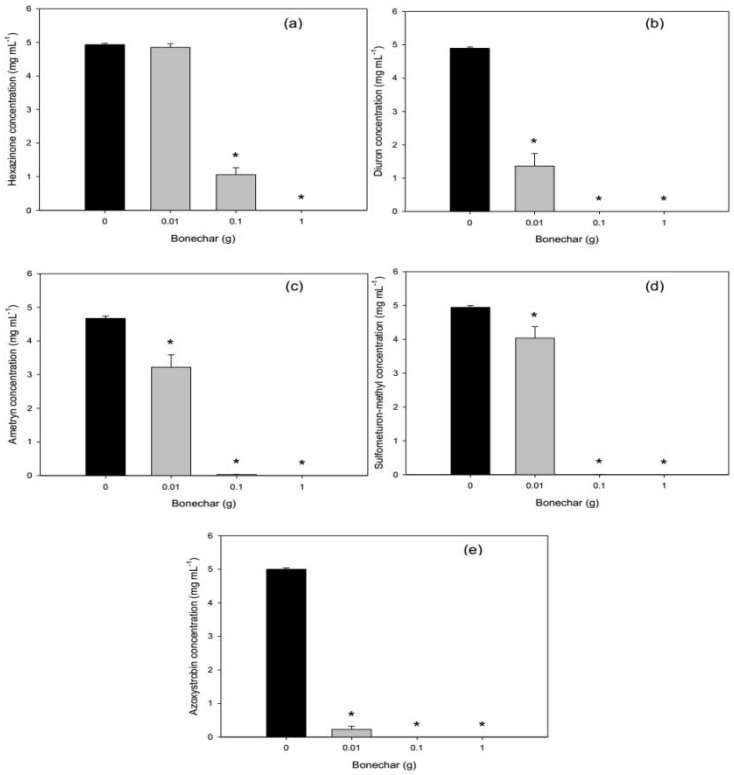


Fig-2: **Concentration (mg mL^{-1}) of hexazinone (a), diuron (b), ametryn (c), sulfometuron-methyl (d), and azoxystrobin (e) in drinking water with different amounts of animal bonechar added (0.01, 0.1, and 1 g) at 1 and 7 d after application (average data). Black bars indicate pesticide concentrations from the water-only systems. Gray bars indicate pesticide concentrations from the bonechar added water systems. Stars above the gray bars indicated which pesticide concentrations from the bonechar added drinking water are significantly different from pesticide concentrations of the drinking water without bonechar (Dunnett's test at $p<0.05$). The vertical lines associated with each bar represent the standard deviation (±SD) of each mean value ($n = 3$).**

Several studies have reported that adsorption by bonechar is associated with surface area properties [27-29] Besides surface area properties that may be related to the chemisorption process, the carbon structure in bonechar likely influences the "physical" adsorption [30] because such adsorption takes place on both the carbon and hydroxyapatite surfaces [31]. The latter authors showed that adsorption by bonechar approaches zero as the carbon content decreases, suggesting that carbon surface is plays an important role in adsorption of organic molecules, such as pesticides. In our study, as bonechar amounts increased, so did pesticide adsorption (Figure 2). The same was observed for adsorption of arsenic and mercury ions with increasing amounts of bonechar [16,32]. The efficiency increase of pesticide removal might be attributed to the fact that the increasing adsorbent doses means an increase in adsorbent surface area, and consequently, more adsorption spots are available for the solute to be adsorbed.

Our results showed that pesticide removal by the addition of bonechar in contaminated drinking water followed the order: azoxystrobin > diuron > ametryn > sulfometuron-methyl > hexazinone, with azoxystrobin presenting the maximum adsorption by bonechar and

hexazinone the lowest adsorption. With the lowest bonechar amount (0.01 g), there was no hexazinone removal whatsoever. However, removal of this pesticide was about 78% and 100% with 0.1 g and 1 g of bonechar added to the water samples, respectively (Figure 2a). Because hexazinone is a herbicide with high solubility in water (33,000 mg L^{-1}) and low adsorption (K_{oc} = 54 L Kg^{-1}) (Table 1), hexazinone is easily leached along the soil profile, as already showed by Close *et al*. [33] and Mendes *et al.* [22]. These authors found that hexazinone has the potential to contaminate both groundwater and surface water. In view of the above, several authors have found efficient techniques for the removal of hexazinone in water, e.g., addition of pre-oxidation with chlorine and chlorine dioxide, granular activated carbon [34,35], functionalized organobentonites [36], and microbial bioreactors [37]. Our study proposes the addition of bonechar to contaminated waters as an alternative method not only for hexazinone removal, but also to diuron, ametryn, sulfometuron-methyl, and azoxystrobin removal.

Diuron removal was about 72%, 100%, and 100% with the addition of 0.01 g, 0.1 g and 1 g of bonechar, respectively (Figure 2b). Azoxystrobin removal was about 96%, 100%, and 100%, with the same increasing bonechar amounts (Figure 2e). In both cases, diuron and azoxystrobin concentrations for all treatments were lower than the control (without addition of bonechar). Although those pesticides do not dissociate when in solution, and have low solubility (Table 1), the interaction with bonechar occur probably by electrostatic interactions, such as van der Waals forces and hydrogen bonds between the pesticides and the carbon from the bonechar.

For example, biochar application in soil increased the adsorption coefficient for diuron [38,39]. In these studies, the authors considered that the retention of diuron occurs through charges generated by the oxidation of the polycondensed aromatic structures of the biochar. The aromatic structures make the biochar surface to turn hydrophobic and therefore enhance diuron adsorption through hydrophobic interaction on surface and through π-π interactions (a type of non-covalent interaction that involves π systems) between the aromatic ring of diuron molecule and the basal planes of the biochar surface [40].

The herbicide diuron possesses high K_{oc} value (813 L Kg^{-1}), and therefore, low potential leaching (Table 1). Despite that, diuron can be carried by runoff and reach surface water. Studies reported that total losses of diuron in surface runoff during the wet season were between 1.3% and 3% [41] and above 0.6% [42] of the amount applied. Therefore, remedying water contaminated with not only the pesticides with greater leaching potential than diuron, but also pesticides with low leaching potential (e.g., diuron) is essential for consumption human and decreases the negative impacts on sensitive aquatic species.

In this study, azoxystrobin was the pesticide most asorbed by bonechar, which was very efficient in removing azoxystrobin from drinking water, even in the lowest amount. However, biochar did not affect azoxystrobin adsorption in another study [43]. Thus, a non-ionizable pesticide (e.g., azoxystrobin), the presence of polarity could justify the adsorption mechanism via hydrogen bonds and the adsorption mechanism occurs via the hydrophobic partition through physical partitioning with the hydrophobic surfaces of the bonechar.

Removal of ametryn was about 31%, 99%, and 100%, with bonechar amounts of 0.01, 0.1, and 1 g added to the water, respectively (Figure 2c). Sulfometuron-methyl removal in water with the lowest, intermediate and high doses of bonechar was about 18%, 100%, and 100%, respectively (Figure 2d). The adsorption of ametryn by bonechar could be explained because chemical interactions between the bonechar functional groups and this pesticide take place when they are present in the same solution that is a heterocyclic ring π electron donor. Aromatic amine cations such as ametryn, can act as π acceptors, forming electron donor−acceptor (π+ −π) interactions with the π electron-rich and the polyaromatic surface of pyrogenic carbonaceous materials [44], such as bonechar. In other studies in which biochar was tested as a pesticide adsorbent compound, increases in ametryn adsorption and other aromatic amines were found compared with the absence of bonechar [44,45].

There are no studies so far evaluating the adsorption of sulfometuron-methyl by biochar and bonechar. This pesticide had a high groundwater ubiquity score (GUS) index (Table 1), which indicates that sulfometuron-methyl has the potential to contaminate water resources because of its higher leaching potential in soils [22]. Therefore, techniques for removing sulfometuron-methyl from drinking water have an important implication for human consumption.

CONCLUSIONS

Cow bonechar adsorbed the pesticides hexazinone, diuron, ametryn, sulfometuron-methyl, and azoxystrobin from contaminated drinking water. The method used in this study was practical, indicating that the use of bonechar for pesticide removal from drinking water could be used in large-scale in water treatment plants or in domestic filters. Our results indicate that bonechar has the potential for pesticide removal from water resources. Research on bonechar use should be funded in order to optimize methodologies for reducing environmental impacts of pesticides in drinking water.

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