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Article

Adsorption Isotherms of Diuron and Hexazinone in Drinking Water Using Four Agro-Industrial Residues

Isotermas de Adsorção de Diuron e Hexazinone em Água Potável Utilizando Quatro Resíduos Agroindustriais

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ABSTRACT - Materials with high organic carbon content are studied for the removal of herbicides from water, such as activated carbon. Low cost alternatives should be investigated for the substitution of this type of material in the removal of herbicides from water. In this context, the aim of this research was to evaluate four agro-industrial residues (white grape bagasse, corn straw, peanut shell and soybean hull) as adsorbents of diuron and hexazinone in drinking water. Samples of drinking water were collected from sources used for human consumption. Five concentrations (1, 2, 3, 4 and 5 mg mL^{-1}) of each herbicide were added to the potable water samples. Each experimental unit consisted of 10 mL of a solution of water and herbicide with 0.1 g of each agro-industrial residue. Sorption was evaluated using the batch equilibrium method. High performance liquid chromatography (HPLC) was used to determine the amount of herbicide present in the aqueous solution. The K$_f$ (Freundlich coefficient) of diuron was higher (2.99-11.93 mmol$^{(1-1/n)}$ L$^{1/n}$ kg^{-1}) than hexazinone (2.31-4.61 mmol$^{(1-1/n)}$ L$^{1/n}$ kg^{-1}) for all adsorbents used. Diuron percentage sorption was higher with white grape bagasse (51.15%) and peanut husk (52.44%), and hexazinone with corn straw (22.77%) and white grape marc (21.48%), than other agro-industrial waste for both herbicides. Even though the sorption of diuron was more pronounced than that of hexazinone, the sorption values obtained in this study were less than 52.44% and considered unsatisfactory in terms of effective removal from contaminated water.

Keywords: herbicide retention, adsorbents, water remediation, environmental risk.

RESUMO - O uso de materiais com alto teor de carbono orgânico vem sendo estudado para a remoção de herbicidas em água, como o carvão ativado. Poucas alternativas de baixo custo são investigadas para a substituição desse tipo de material na remoção de herbicidas em água. Nesse contexto, o objetivo desta pesquisa foi avaliar resíduos agroindustriais (bagaço de uva branca, palhada de milho, casca de amendoim e casca de soja) como adsorventes do diuron e hexazinone em água potável. Amostras de água potável foram coletadas de fonte para o consumo humano. Foram adicionadas cinco concentrações (1, 2, 3, 4 e 5 mg mL^{-1}) de cada herbicida em amostras de água potável. Os tratamentos consistiram em 10 mL da solução de água e herbicidas com 0,1 g de cada resíduo agroindustrial. A sorção foi avaliada utilizando o método do equilíbrio em batelada. A cromatografia líquida de alta eficiência (HPLC) foi utilizada para determinar a quantidade restante de herbicida em solução. O K$_f$ (coeficiente de Freundlich) para o diuron foi mais pronunciado (9,94-11,93 mmol$^{(1-1/n)}$ L$^{1/n}$ kg^{-1}) do que para o hexazinone (2,31-4,61 mmol$^{(1-1/n)}$ L$^{1/n}$ kg^{-1}) em todos os adsorventes. A sorção percentual de

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diuron foi maior com bagaço de uva branca (51,15%) e casca de amendoim (52,44%), e a do hexazinone, com palha de milho (22,77%) e bagaço de uva branca (21,48%), em comparação com outros resíduos agroindustriais dos dois herbicidas. Embora a sorção de diuron tenha sido mais pronunciada que a de hexazinone, os valores de sorção obtidos neste estudo foram inferiores a 52,44% e considerados insatisfatórios em termos de remoção eficaz da água contaminada.

Palavras-chave: retenção de herbicidas, adsorventes, remediação da água, risco ambiental.

INTRODUCTION

Herbicide residues found in spring water are commonly derived from the leaching, runoff and volatilization of the compounds applied in agricultural areas and/or from places where washing of packaging is performed. Among the pesticides, the class of herbicides is the most widely used in the world and, in Brazil, are frequently detected in water sources beyond the areas of application (Oliveira Jr et al., 2001; Santos et al., 2013). In Brazil, the contamination of water by pesticides is the second major cause of contamination of water resources after domestic sewage (IBGE, 2011). In view of this, the concern with potability has stimulated research on the remediation of herbicide residues in water, mainly using alternative adsorbent materials derived from organic residues (Gonçalves Jr, 2013; Silva et al., 2013; Mendes et al., 2017)

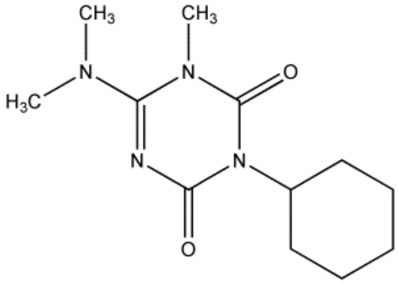
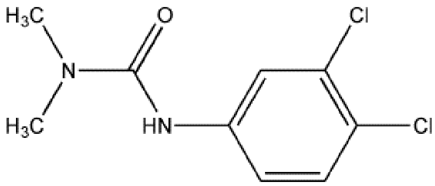
In areas of sugarcane crops, the effect may be even more pronounced because it is one of the crops where chemical management of weed control is most used (Vivian et al., 2007). A diuron + hexazinone mixture is commonly used in sugarcane crops for a wider spectrum of control (Kruse et al., 2000). Diuron can move to watercourses through surface runoff loaded with soil particles to which it binds, even with low solubility in water (35.6 mg L^{-1} at 20 ^{o}C) (PPDB, 2018). Inoue et al. (2008) reported the movement capacity of this herbicide within soil, in intense volumes of precipitation (> 60 mm), in soil with lower clay content (100 g kg^{-1}) and organic matter (5.19 g dm^{-3}). In Brazil, Britto et al. (2012) found diuron residues (0.9 µg L^{-1}) in the Poxim River that supplies the city of Aracaju in the State of Sergipe. With regard to hexazinone, residues in water have been found due to its high leaching potential (GUS 4.43) and high solubility in water (33000 mg L^{-1} at 20 ^{o}C) (PPDB, 2018). The physico-chemical characteristics of herbicides may indicate different behaviors in the environment; these properties are presented in Table 1.

Armas et al. (2007) found hexazinone residues (0.5 µg L^{-1}) in the Corumbataí River, which is part of a hydrographic supply network in the State of São Paulo, Brazil. In Brazil, there are no maximum residue limits allowed for both herbicides (Brasil, 2005). According to Orlando et al. (2014), diuron was detected in 72% and hexazinone in 100% of the Sacramento-San Joaquin River delta surface water samples in California, with a maximum detected concentration of 0.695 µg L^{-1} of 0.984 µg L^{-1}, respectively for diuron and hexazinone. Maximum permissible residue levels in the United States, which are set to prevent adverse health effects, are 100 µg L^{-1} for diuron and 2000 µg L^{-1} for hexazinone (PAN, 2018).

The presence of herbicide residues in water can lead to contamination and toxicological effects in organisms. Studies have reported the killing of algae (Perschbacher and Ludwig, 2004) and effects on oyster gametogenesis (Akcha et al., 2016; Rondon et al., 2016) in the presence of diuron. Changes in the phytoplankton community and decrease in zooplankton and micro-invertebrate species have been reported with chronic exposure to diuron and hexazinone (Hasenbein et al., 2017).

Adsorption, photocatalysis and/or advanced oxidation processes can be used as strategies for the removal of herbicides from drinking water (Baird, 2002). Among these, adsorption using biomass from agro-industrial residues (biosorbents) is an advantageous alternative in the sorption of herbicides from water (Hu et al., 2016). These are low cost materials which are generated in large quantities, have limited generation of sludge in environment and have comparable efficiency to conventional adsorbents (Chaukura et al., 2016; Homem et al., 2018). Silva et al. (2013) reported >90% removal efficiency of atrazine and simazine from drinking water using banana peel residues. In this perspective, research into various organic materials, such as

Table 1 - Structural formulas and physicochemical properties of herbicides

Attribute	Hexazinone	Diuron
Structural formula		
Molecular formula	$C_{12}H_{20}N_4O_2$	$C_9H_{10}Cl_2N_2O$
IUPAC name	3-cyclohexyl-6-dimethylamino-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione	3-(3,4-dichlorophenyl)-1,1-dimethylurea
Chemical group	triazinone	phenylurea
Molecular weight (g mol^{-1})	252.31	233.09
Water solubility at 20 °C (mg L^{-1})	33000 (high)	35.6 (low)
Log K_{ow}	1,17 (low)	2,87 (moderate)
pK_a at 25 °C	2.2 (weak base)	no dissociation
Vapor pressure at 25 °C (mPa)	0.03 (low volatility)	1.15 x 10^{-03} (low volatility)
DT50 soil (d)	105 (persistent)	75.5 (moderately persistent)
K_{oc} (L kg^{-1})	54 (mobile)	813 (slightly mobile)
GUS (Groundwater Ubiquity Score) leaching potential index	4.43 (high leachability)	1.83 (transition state)

sunflower seeds, rice hulls, beet pulp and corn cob, has been carried out and satisfactory results have been obtained on the removal of herbicides (trifluralin, glyphosate, diuron and 3,4-DCA) from water (Huguenot et al., 2010; Rojas et al., 2015).

Adsorption of herbicides using alternative materials can be employed directly or in combination with other techniques to improve the efficiency of removal of pollutants from water (Zolgharnein et al., 2011). The investigation of the adsorptive capacity of organic wastes to the herbicides is promising in the remediation of these compounds of the environment. In view this, the objective of this research was to evaluate the retention capacity of the agro-industrial residues, white grape marc, corn straw, soybean hulls and peanut hulls, in adsorbing diuron and hexazinone herbicides from drinking water.

MATERIAL AND METHODS

Drinking water samples

Samples of drinking water were collected directly from a household faucet in Piracicaba, São Paulo, Brazil. The faucet was opened by filling a 1.0 L bottle with the same water supplied to consumers from the city's water supply network as water for human consumption. The vessel was stored for 24 h at room temperature until contamination was initiated. Information provided by the water supply network of the municipality itself was used for details of the physico-chemical properties of the collected water samples (Table 2).

Table 2 - Selected properties of drinking water quality.

Property	Value	Permitted value*
Chlorine (mg L^{-1})	2.7	<5
Fluorides (mg L^{-1})	0.67	<1.5
Iron (mg L^{-1})	0.03	<0.3
Manganese (mg L^{-1})	0.01	<0.1
Turbidity (NTU$^{(1)}$)	0.80	<5
Color (PCU$^{(2)}$)	2	<15
pH	8.1	6.0-9.5
Total coliforms	absent	absent
Fecal coliforms	absent	absent

$^{(1)}$ NTU: nephelometric turbidity units. $^{(2)}$ PCU: platinum cobalt units. * Source: SEMAE (2018).

Herbicides

Stock solutions of diuron and hexazinone were prepared from their analytical standards, with 99.5 and 99.9% chemical purity, respectively (Sigma Aldrich, St. Louis, MO, USA). All stock solutions were prepared at a concentration of 1000 µg mL^{-1} in acetonitrile. Working solutions with five concentrations (1, 2, 3, 4 and 5 µg mL^{-1}) of each herbicide were also prepared. For each treatment, 0.25, 0.5, 0.75, 1.0, 1.25 and 3.15 mL of each working solution was added to 10 mL samples of contaminated drinking water. The five increasing concentrations were used to adjust the adsorption isotherms.

Agro-industrial waste

White grape bagasse, corn straw (crop residue without spikes), peanut shells and soybean hulls were used. All materials were milled and homogenized in a mechanical mill and sieved through a 2 mm mesh. A 0.1 g quantity of each material was added to 10 mL of potable water, previously contaminated with herbicide, in 50 mL Teflon tubes, resulting in a 1:100 w/v mixture. The tubes were sealed with a screw-cap. The characteristics of the residues used in this study are presented in Table 3.

Table 3 **-** Properties physicochemical of agro-industrials waste

Property	White grape bagasse	Corn stalk	Peanut shell	Soybean hull
pH ($CaCl_2$ 0.01 M)	3.6	7.4	4.7	5.2
Density (Organic waste) (g cm^{-3})	0.47	0.20	0.26	0.36
Total Moisture (%)	7.01	12.13	9.6	11.49
Total organic matter (Combustion) (%)	88.33	81.99	88.43	84.22
Organic Carbon (OC) (%)	47.78	44.13	47.63	45.63
Total mineral residue (TMR) (%)	4.67	5.88	1.97	4.28
Total Nitrogen (N) (%)	3.04	0.94	0.93	3.61
Total Phosforo (P_2O_5) (%)	0.69	0.33	0.06	0.43
Total Potassium (K_2O) (%)	1.71	1.23	0.09	1.22
Total Calcium (Ca) (%)	0.44	0.34	0.35	0.60
Total Magnesium (Mg) (%)	0.11	0.23	0.08	0.30
Total Sulfur (S) (%)	0.41	0.28	0.10	0.19
C/N relation	16	47	51	13

Experimental design

The experiment was based on a completely randomized design with a 4×2 factorial scheme, involving four agro-industrial residues (white grape bagasse, corn straw, peanut shelsl and soybean hulls) and two herbicides (diuron and hexazinone). Three replicates were used for each treatment.

Removal of herbicides from water

The adsorption studies were performed at room temperature (20 ± 2 °C) with the agitator set at 200 rpm. After the tubes were shaken for 24 h to achieve horizontal table equilibration, the samples were centrifuged at 7000 rpm for 5 min at 4 °C. Aliquots (1 mL) of supernatants from each vial were filtered through a 300 CW PTFE filter (0.45 µm) for HPLC analysis, so that the supernatant was discarded, leaving only the vegetable residue. The concentration of each herbicide present in each potable water sample was determined. The results were expressed as mg of herbicide per mL of drinking water.

Chromatographic analysis

The chromatographic method used, described by Mendes et al. (2017) with some modifications, was validated and met the requirements of the Brazilian national guidelines (Anvisa, 2012) and the European Union (SANTE, 2016). Chromatographic determinations of the initial and final concentrations (after adsorption) of the herbicides in the samples were performed by HPLC (Agilent Technologies®, model 1200 series), with a UV-Vis detector (Agilent Technologies®) and a C18 column (3.5 × 4.6 × 100 mm di; Kromasi). Chromatographic conditions for analysis were as follows: water (with orthophosphoric acid added) and acetonitrile (40:60 v/v) as the mobile phase; flow rate of 1 mL min^{-1}; injection volume of 20 µL; column temperature of 35 ^{o}C and 242 nm wavelength. Chemstation® software was used for data analysis.

Linear adsorption model

The adsorption coefficients were calculated using the following equation: $K_d = C_s/C_e$, where C_s is the concentration of herbicide adsorbed onto the agro-industrial residue (µmol kg^{-1}) and C_e is the equilibrium herbicide concentration in the liquid phase (µmol L^{-1}). The adsorption data were normalized to the organic carbon (OC) content of agro-industrial waste and K_{oc} was calculated from the sorption adsorption coefficient using the following formula: $K_{oc} = (K_d/\%\ OC) \times 100\%$, where %OC is the percentage of OC in organic materials. The units of K_d and K_{oc} are represented in L kg^{-1}.

Freundlich adsorption isotherm model

The adsorption coefficients, K_f and 1/n, were calculated by the Freundlich isotherms as follows: $C_s = K_f \times C_e^{1/n}$, where C_s is the concentration (mg g^{-1}) of the herbicide sorbed by the soil after equilibration, K_f is the Freundlich equilibrium constant (µmol$^{(1-1/n)}$ L$^{1/n}$ kg^{-1}), C_e is the concentration of herbicide (mg L^{-1}) after equilibrium in solution, and 1 n is the degree of linearity of the isotherm. The normalization of these values for the organic carbon (OC) content of the agro-industrial wastes was performed, so that the K_{foc} was calculated from the Freundlich equilibrium constant, using the following formula: $K_{foc} = (K_f\ /\%OC) \times 100\%$, where % OC is the percentage of OC in organic materials. The units for K_f and K_{foc} are represented in µmol$^{(1-1/n)}$ L$^{1/n}$ kg^{-1}.

Statistical analysis

The adsorption data for diuron and hexazinone were adjusted for linear and non-linear regressions by the Freundlich model, as previously described. Figures were plotted using Sigma Plot® (version 10.0 for Windows, Systat Software Inc., Point Richmond, CA, USA).

RESULTS AND DISCUSSION

Validation of the chromatographic method

The areas of the chromatographic peaks and the applied concentrations were used to determine the following validation parameters: selectivity, linearity, limit of detection (LOD), limit of quantification (LOQ), and precision and accuracy of the method. These parameters indicated the reliability of the method used (ANVISA, 2012; SANTE, 2016). The selectivity or identification of each herbicide contained in the samples was by means of the retention time for each one; this was 4.44 min for hexazinone and 5.36 min for the diuron. At concentrations of 1, 2, 3, 4 and 5 µg mL^{-1} for both hexazinone and diuron, the correlation coefficient (R^2) was higher than 0.99. The calibration curves generated were $y = 65.08308x + 10.45979$ for hexazinone and $y = 86.52990x + 9.67090$ for diuron. The LOD was 0.1 µg mL^{-1} and the LOQ was 0.2 µg mL^{-1} for the two herbicides. These limits indicate the minimum level of detection of the substances by the equipment and the precision of the quantification, respectively Values above 99% were recovered (Table 4), consistent with the values determined by ANVISA (2012) and SANTE (2016); the recovery percentage (R%) was 70-120% and coefficient of variation (CV%) <20.

Table 4 **-** Recovery levels (3 injections of each replicate) of the proposed method for the herbicides (5.0 μg ml^{-1}) in drinking water samples

Herbicide	Sample								
	1st			2nd			3rd		
	R(%)(1)	± SD(2)	CV (%)(3)	R (%)	± SD	CV (%)	R (%)	± SD	CV (%)
Hexazinone	95.56	0.00	0.00	99.74	0.01	0.00	100.09	0.02	0.00
Diuron	99.54	0.05	0.01	99.33	0.08	0.02	99.40	0.06	0.01

(1) R(%): recovery percentage. (2) SD: standard deviation. (3) CV: coefficient of variation.

Adsorption isotherms of hexazinone and diuron in drinking water with four agro-industrial residues

The high coefficient of determination for the linear model (R^2> 0.93) and the significant variables indicated the reliability of the results provided by this model (Table 5). The values of the partition coefficient K_d (linear model) for hexazinone with agro-industrial waste were in the range 0.40-1.64 L kg^{-1}. For diuron, the sorption values were 2.85-8.61 L kg^{-1} This normalized coefficient for the OC content of agro-industrial waste (K_{oc}) indicated higher retention hexazinone and diuron with white grape bagasse (37.79 and 178.92 L kg^{-1}, respectively) than other agro-industrial waste. This organic material had a higher OC content (47.78%) than the others (Table 3). In relation to materials with high OC content, Rojas et al. (2014) indicated the high potential of rice husk for sorption of simazine in solution (K_{oc} = 194 L kg^{-1}); using 1 g of the material resulted in 73.8% maximum adsorption of the herbicide due to its OC of 46.21%, which is similar to the OC of white grape marc used in this study.

Table 5 **-** Linear adsorption parameters for the hexazinone and diuron to agro-industrial waste in drinking water

Herbicide	Agro-industrial waste	K_d	K_{oc}	R^2	*p*
		(L kg^{-1})			
Hexazinone	White grape bagasse	1.52 ± 0.30(1)	37.79 ± 6.30	0.94	0.0194
	Corn straw	0.40 ± 0.07	8.97 ± 1.64	0.99	0.0011
	Peanut shell	0.58 ± 0.04	12.20 ± 0.94	0.93	0.0209
	Soybean hull	1.64 ± 0.10	35.04 ± 2.19	0.95	0.0136
Diuron	White grape bagasse	8.61 ± 1.91	178.92 ± 39.92	0.95	0.0145
	Corn straw	7.04 ± 0.38	151.00 ± 8.58	0.94	0.0156
	Peanut shell	7.32 ± 0.60	53.04 ± 12.62	0.96	0.0110
	Soybean hull	2.85 ± 0.98	62.19 ± 21.45	0.95	0.0137

(1) Values are included in the mean and standard deviation (SD) of the mean (*n* = 3).

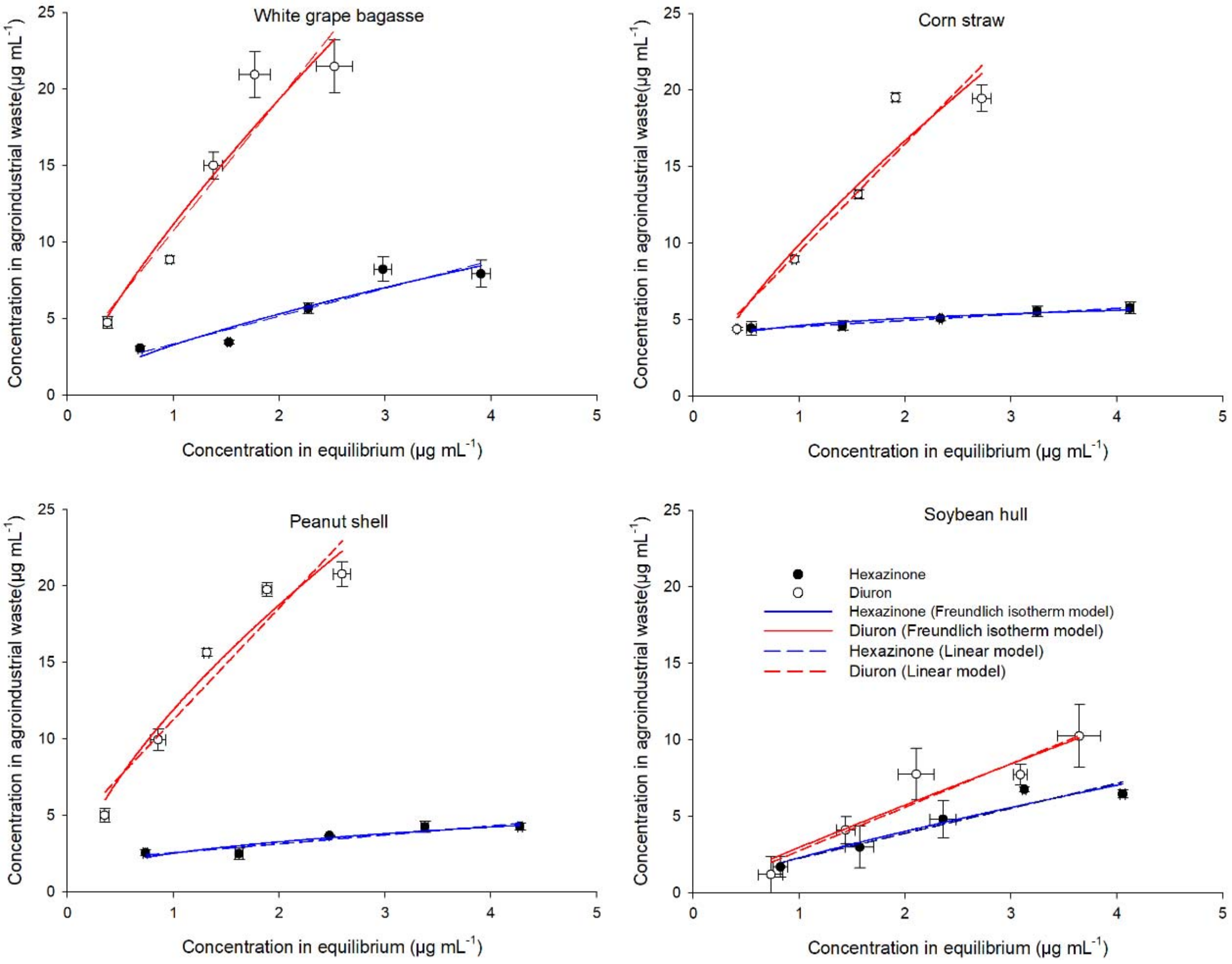
The Freundlich equation was adequate for describing the adsorption of hexazinone and diuron at agro-industrial waste from drinking water (R^2> 0.92) (Table 6). The values of 1/n for hexazinone were in the range 0.14-0.81 and 0.66-0.95 for diuron, indicating the behavior of adsorption isotherms of type L (1/n <1) (Giles et al., 1960). That, according to Limousin et al. (2007), represents the progressive saturation of the adsorption matrix. The Freundlich isotherms showed a very similar behavior to the linear model (Figure 1), indicating that the adsorption of these herbicides by organic materials can be explained by the two models, in which increased adsorption to organic residues rises with increasing concentrations of the herbicides.

As for the adsorptive capacity of the organic residues, after adjustment to the Freundlich model, K_f values were lower for hexazinone (2.31-4.61 μmol $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}) than for the diuron (2.99-11.93 μmol $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}) with all materials (Table 6). Soybean hulls presented K_f values of 2.31 and 2.99 μmol $^{(1-1/n)}$ $L^{1/n}$ kg^{-1} for hexazinone and diuron, respectively, similar for both herbicides, while the other materials were better adsorbents for diuron ($p < 0.05$) (Table 6). When the K_f values were adjusted to the OC content of the agro-industrial waste, notable herbicide

Table 6 **-** Freundlich adsorption parameters for the hexazinone and diuron to agro-industrial waste in drinking water

Herbicide	Agro-industrial waste	K_f	K_{foc}	1/n	R^2	*p*	Adsorption (%)
		($\mu mol^{(1-1/n)}$ $L^{1/n}$ kg^{-1})					
Hexazinone	White grape bagasse	3.29 ± 0.39[1]	68.83 ± 8.09	0.69 + 0.14	0.94	0.0196	21.48
	Corn straw	4.61 ± 0.18	104.69 ± 4.16	0.14 ± 0.04	0.95	0.0135	22.77
	Peanut shell	2.53 ± 0.06	53.11 ± 1.21	0.37 ± 0.02	0.92	0.0266	14.40
	Soybean hull	2.31 ± 0.55	50.45 ± 11.98	0.81 ± 0.14	0.96	0.0108	16.27
Diuron	White grape bagasse	11.20 ± 1.38	232.51 ± 28.96	0.79 ± 0.25	0.95	0.0114	51.15
	Corn straw	9.94 ± 1.17	212.00 ± 3.87	0.75 ± 0.05	0.95	0.0114	46.51
	Peanut shell	11.93 ± 1.23	250.60 ± 4.81	0.66 ± 0.04	0.98	0.0047	52.44
	Soybean hull	2.99 ± 0.73	66.31 ± 15.90	0.95 ± 0.33	0.95	0.0133	20.94

(1) Values are included in the mean and standard deviation (SD) of the mean ($n = 3$).



The vertical bars associated with each symbol represent the standard deviation (± SD) of each mean value of the concentration selected from the agro-industrial residue ($n = 3$) and the vertical bars associated with each symbol represent the standard deviation (± SD) mean of the equilibrium concentration in the solution ($n = 3$).

Figure 1 **-** Freundlich adsorption and linear isotherms of hexazinone and diuron in agriculture waste in the drinking water.

adsorption values were reported for corn straw with hexazinone (K_{foc} = 104.69 $\mu mol^{(1-1/n)}$ $L^{1/n}$ kg^{-1}) and peanut shells with diuron (K_{foc} = 250.60 $\mu mol^{(1-1/n)}$ $L^{1/n}$ kg^{-1}).

In general, the adsorption percentages of the residues were 2.38, 2.04, 3.64 and 1.29 times higher for white grape marc, corn straw, peanut shell and soybean hull, respectively, with diuron when compared to hexazinone. This is due to diuron being more apolar (log K_{ow} 2.87) and hexazinone being less apolar (log K_{ow} 1.17), which gives for the first a higher adsorption affinity with OC present in the organic residues (Table 1). The materials with the highest percentage of adsorption were white grape bagasse and peanut shells (51.15 and 52.44%, respectively) with diuron. Rojas et al. (2014), studying the removal of different herbicides from water by organic materials, indicated that the adsorption capacity of atrazine and alachlor increased with the hydrophobic character of each and decreased with the solubility of the molecule. In the case of a hydrophobic herbicide similar to diuron, Rodríguez-Cruz (2012) reported high adsorption of linuron using grape marc (Kf = 92.9 µg mL^{-1}) when applied to the soil. Similarly, Marín-Benito et al. (2014) also found greater retention and reduction in leaching of linuron by adding organic materials to the soil, such as grape bagasse.

With the intention of removing this herbicide from drinking water, our results indicated 22.77% of hexazinone adsorption with corn straw and 21.48% with white grape bagasse. However, hexazinone adsorption values were low relative to diuron. Due to the high solubility of hexazinone (33,000 mg L^{-1} at 20 °C) it is often found in bodies of water in Brazil (Santos et al., 2013). In this view, other materials are reported in the literature to be adsorbents of this herbicide from drinking water, such as bonechar (biochar derived from bovine bones) indicated by Mendes et al. (2017), also using drinking water. The authors found 78% and 100% removal of hexazinone with 0.1 g and 1 g of bonechar, respectively, when added to 10 mL of drinking water containing the contaminant. Another means of removing this herbicide was reported by Hunter and Shaner (2012), using microbial aerobic reactors (nitrogen limited) with sand that stimulate microbial growth; this removed more than 95% of hexazinone from the water, being able to remediate high quantities of the herbicide (100 mg L^{-1}).

The different ways in which agro-industrial waste can be used present several possibilities. They may be related to herbicide retention and/or induction of microbiota activation and degradation of these compounds are interesting. Biobed systems are used to reduce the leaching of some phenylureas, such as linuron, diuron and methabenzthiazuron, in the biopurification of the waters used in agriculture, especially during the washing of application tanks (Spliid et al., 2006). Another use is in filtration systems in continuous water flow systems, replacing activated carbon. Dantas et al. (2009) indicated higher adsorption affinity of diuron to activated carbon than that of hexazinone in this type of system. However, not all materials containing large amounts of carbon may be indicated in herbicide removal, as in the case of the four materials tested in this study, even using these systems. In general, hexazinone reached a maximum adsorption of only a quarter of the total applied (mean of concentrations), already the half-dose applied diuron. This finding indicates that the quantities removed by agro-industrial waste are insufficient for the effective removal of the herbicides from water in which these contaminants are present.

Of the agro-industrial wastes used in this study, white grape marc, peanut hulls and corn straw showed higher retention of the herbicides diuron and hexazinone from drinking water. However, the adsorbed amounts were not sufficient for the total removal of these contaminants from potable water. We demonstrated the potential of white grape marc for apolar herbicides, which present greater risks to the environment when they reach groundwater and surface water. Investigations of the potential retention and optimal use of agro-industrial wastes, which are abundant and are associated with low cost, are essential to reducing the environmental impact of herbicides and pesticides in general.

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