Revista Brasileira de Geografia Física
ISSN:1984-2295
Homepage: https://periodicos.ufpe.br/revistas/rbgfe

The Use of Biochar in Reducing Contamination of Soils in Agreste Region of Pernambuco by Sulfamethoxazole and Sulfadiazine

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Artigo recebido em 08/02/2024 e aceito em 03/09/2024

A B S T R A C T
Around 30 to 90% of administered antibiotics are not fully metabolized and, therefore, pose risks to the quality of groundwater. In this way, the objective was to understand the sorption behavior of SDZ and SMX, in sandy soil from the Agreste of Pernambuco, to reduce the contamination of groundwater. For this, batch tests were carried out on soils collected in Agreste Pernambuco in two extracts, one at 0 - 20 cm and the other at 20 - 40 cm deep, with and without the addition of biochar. The results showed that the addition of biochar to the soil led to an increase in sorption of both SDZ and SMX, reaching approximately 73 and 123 mg kg^{-1}, in the case of soil from the 0 - 20 cm layer, respectively. In the case of the 20 - 40 cm layer, SDZ sorption exceeded 102 mg kg^{-1}, while for SMX it exceeded 95 mg kg^{-1}. Furthermore, the reaction equilibrium times for SDZ and SMX were the same in the case of soils from the same layer, with or without the addition of biochar however, in the case of SMX, these times were shorter (12h). It was also noted that at low pH values (pH < 4) the sorption of the two antibiotics is greater, showing a dependence of sorption on the pH of the solution. As a result, it became clear that these antibiotics have high mobility, indicating an imminent risk of contamination of soil surface, and groundwater.
Keywords: Antibiotics, Emerging Contaminants, Soil Remediation, Filter Layer

O Uso do Biochar na Redução da Contaminação de Solos do Agreste Pernambucano por Sulfametoxazol e Sulfadiazina

R E S U M O
Cerca de 30 a 90% dos antibióticos administrados não são totalmente metabolizados e por isso eles vem representando riscos para a qualidade das águas subterrâneas. Deste modo, o objetivou-se compreender o comportamento da sorção do SDZ e SMX, em um solo arenoso do Agreste de Pernambuco, para reduzir a contaminação das águas subterrâneas. Para isso, foram realizados ensaios em batch de solos coletados no Agreste pernambucano em dois extratos, um de 0 - 20 cm e outro de 20 - 40 cm de profundidade, com e sem a adição de biochar. Os resultados mostraram que a adição do biochar ao solo propiciou um aumento na sorção, tanto do SDZ quanto do SMX, chegando a aproximadamente 73 e 123 mg kg^{-1}, no caso do solo da camada de 0 - 20 cm, respectivamente. Já no caso da camada de 20 - 40 cm, a sorção do SDZ ultrapassou os 102 mg kg^{-1}, enquanto que para o SMX ultrapassou os 95 mg kg^{-1}. Ademais, os tempos de equilíbrio das reações para o SDZ e SMX foram os mesmos no caso dos solos de mesma camada, com ou sem a adição do biochar, entretanto no caso do SMX estes tempos foram menores (12h). Também se notou que para valores de pH baixos (pH <

4) a sorção dos dois antibióticos é maior, mostrando uma dependência da sorção com relação ao pH da solução. Com isso, evidenciou-se que estes antibióticos possuem uma alta mobilidade, indicando um risco iminente de contaminação do solo e das águas superficiais e subterrâneas.
Palavras-chave: Antibióticos, Contaminantes Emergentes, Remediação do Solo, Camada Filtrante.

Introduction

In addition to concerns about availability, water quality has become an urgent issue worldwide, particularly in semi-arid regions. The use of anthropogenic chemicals, classified as emerging pollutants, further aggravates this problem, since they are not regulated and have a potential impact on human and environmental health (González-Acevedo; García-Zarate; Flores-Lugo, 2019).

Emerging contaminants (ECs) are toxic products that are not removed by conventional water treatment processes. These include endogenous and synthetic hormones, contraceptives, antibiotics, anti-inflammatories, insecticides, herbicides, and cleaning and personal hygiene products (Empresa Basileira de Pesquisa Agropecuária - EMBRAPA, 2018).

Antibiotics are becoming a global concern as they are being found inappropriately in the environment and can cause serious negative impacts on human and ecological health (Cid et al., 2020; Li et al., 2023). These drugs have been widely used for the treatment and prevention of diseases in animals and humans (Rodriguez-Mozaz et al., 2015; Brooks et al., 2023). Once administered, part of the dosages are not completely metabolized and end up being eliminated through urine and feces that makeup manure (Zhang et al., 2019; Juela et al., 2021), which is widely used as fertilizer in agricultural soils. (Spielmeyer et al., 2020, Ibekwe et al., 2023).

Around 30 to 90% of these antibiotics are not fully metabolized and therefore appear as emerging contaminants that have been disseminated into the environment through fertilization or irrigation of soil, urban wastewater, and sediments, posing risks to crops, ecosystems soil and groundwater quality (Du & Liu, 2012; Juela et al., 2021). According to Guo et al. (2014), the excretion of these unmetabolized antibiotics in the feces and urine of humans and animals is one of the main sources of introduction of these antibiotics into the aquatic ecosystem.

Due to this wide applicability, its high efficiency and low production costs, the Sulfonamides (SAs) are considered one of the most widely used classes of antibiotics in human and veterinary medicine (Zheng et al., 2013), and have a high degree of ionization and mobility in water and soil (Dong et al., 2021; Hu, Zhou & Luo, 2010; Kwon et al., 2011; Vithanage et al., 2015; Zhang et al., 2017), sulfadiazine (SDZ) and sulfamethoxazole (SMX) being representatives of the class of SAs with higher concentrations in the environment (Yan et al., 2013; He et al., 2019; Lyu et al., 2020), reaching 91 mg kg^{-1} of SDZ (Marténez-Carballo et al., 2007) and 1.1 µg L^{-1} of SMX in groundwater (Barnes et al., 2008).

The southern Agreste region of Pernambuco is an important dairy basin in the state and has great potential in the production of animal manure as a by-product. However, when used to fertilize sandy soils in this region, which have low adsorption capacity, this by-product of dairy farming can cause contamination of surface and groundwater by unmetabolized antibiotics (Qi et al., 2023). Therefore, it is necessary to create mechanisms such as the use of filtering layers (Biochar (BC), zero valence ions and zeolites) that increase the retention of these pollutants in the soil (Gupt et al., 2020; Budania & Dangayach, 2023; Pradhan et al., 2023).

BC is a carbon-rich coal derived from the pyrolysis of biomass, in anaerobic conditions or where there is little oxygen (Beesley; Marmiroli, 2011; Cheng et al., 2019), which is used in agriculture to increase soil fertility and create a carbon sink to mitigate environmental pollution from many compounds (Pandit et al., 2018; Nguyen et al., 2023).

The temperatures used in pyrolysis can vary from 200 to 1000 °C and burnings carried out above 500 °C generate pyrolytic organic matter with a highly aromatic and more stable carbon structure, with a large specific surface area and high carbon contents (depending on the type of organic matter), ranging from 0.5 to 450 m^2 g^{-1}, giving it high porosity and a high sorption capacity, especially of compounds that are poorly soluble in water (Khan, et al., 2013; Hansen et al., 2015; Brassard et al., 2016; Pandit et al., 2018).

Furthermore, the use of BC as an adsorbent material for contaminant removal has been gaining immense interest in research, so that it has also been used to increase the retention of pharmaceuticals, microplastics, organic contaminants and mitigate the problems caused by climate change (Beesley e Marmiroli, 2011; Peiris et al., 2017; Siipola et al., 2020; Gomes et al., 2022; Blenis et al., 2023; Bousdra, Papadimou & Golia, 2023), due to the low cost and adsorption properties (Ahmad et al., 2014; Gomes et al., 2022).

Although biochar has been used in many

studies in recent years, there is still a certain gap in how to apply it effectively to a particular circumstance of environmental contamination (Lap et al., 2021).

The application of BC can bring significant changes in soil properties, altering its structure, porosity, consistency, pore diameter, particle size distribution, and density, due to a larger specific surface area (Hansen et al., 2015; Brassard, Godbout & Raghavan, 2016; Pandit et al., 2018), contributing to a greater water retention capacity in sandy soils (Carvalho & Santos, 2016), in addition to the emergence of reactive sites (Brady & Weil, 2008; Naidu & Birke, 2015).

Thus, several authors (Dong et al., 2021; Gong et al., 2022; Chen et al., 2023; Zhang et al., 2023) showed that SDZ and SMX can be found in surface, subsurface and sewage treatment plants and that BC can be used to remove these. However, although there are many studies on the removal of SAs in the literature, there is still a large gap regarding the mechanisms of interaction between BC and these antibiotics (Sen et al., 2023; Peiris et al., 2017). In this context, the objective was to understand the sorption behavior of antibiotics, SDZ and SMX, in sandy soil in Agreste of Pernambuco, to reduce the contamination of groundwater and surface waters.

Materials and methods

Study área

The study area is located in the municipality of São João, belonging to the microregion of Garanhuns, within the southern Agreste mesoregion of the state of Pernambuco (Figure 1). Garanhuns has an area of 485 thousand km² and throughout its development in the 20th century, it went through two major cycles, the first being related to the development of coffee production and the second, and more recent, to dairy production (Chaves, 2023).

Garanhuns is responsible for a large portion of dairy production in the state of Pernambuco, having been responsible for the production of more than 2 million liters per day (Silva et al., 2019).

Soil characterization

The deformed soil samples were collected in two distinct layers (0 - 20 and 20 - 40 cm) within the same soil profile. Subsequently, in the laboratory, the samples were air-dried, crumbled and then the soil was sieved using a mesh with 2 mm internodes to be used in batch tests. The most superficial layer of the soil (0 - 20 cm) has a granulometric composition that is mainly sandy, with 77.08%, 9.37% clay, and 13.55% silt, being classified as sandy loam. The second soil layer (20 - 40 cm) also has a mostly sandy layer, containing an even higher percentage of sand than the previous layer (81.47%), while the percentage of clay is 4.69% and that of silt was 13.84%, being classified as loam sand.

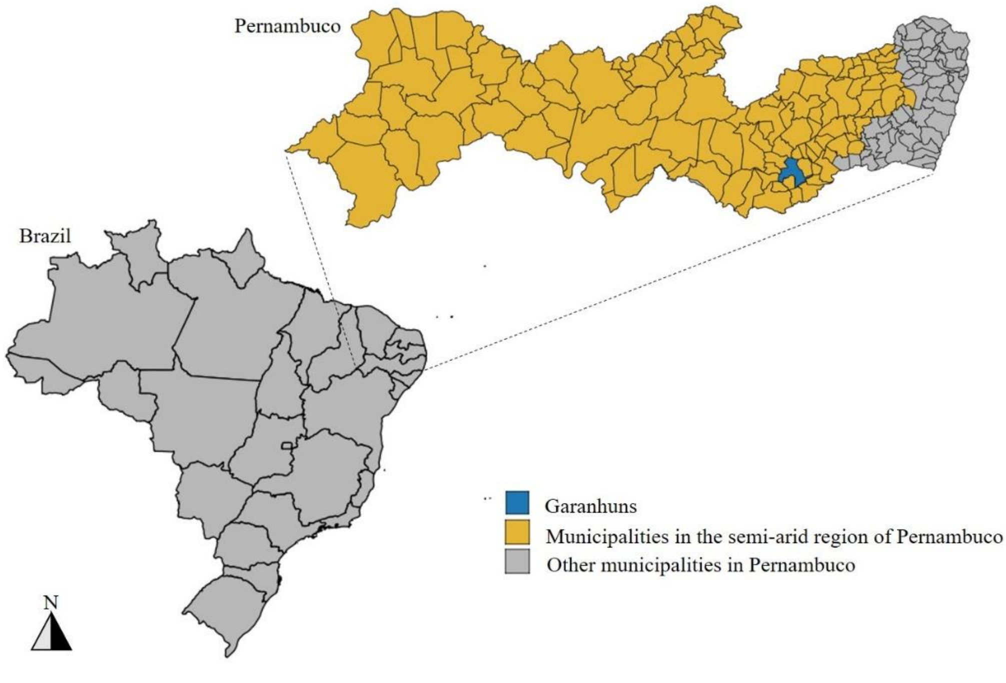

Figure 1. Municipality where soil collections were carried out.

Biochar

To carry out the laboratory tests, the biochar used was produced from coffee husks, from an agribusiness in Garanhuns and supplied by Lima et al. (2018). This raw material was subjected to 530 °C for 10 - 12 h in low amounts of oxygen. The material produced was then analyzed and its physical-chemical characteristics are pH = 10.31, specific surface area = 244 m^2 g^{-1}, carbon = 67.11%, nitrogen = 2.05%, and cation exchange capacity 22.54 (Lima et al., 2018). In this study, samples containing soil plus biochar had a mass ratio (M:M) of 5%.

Antibiotics

Sulfadiazine (SDZ) and Sulfamethoxazole (SMX) are two antibiotics from the sulfonamide class and have molar masses equal to 250.28 e 253.28 g mol^{-1}, respectively. SDZ has a melting point of 526 K, a density of 1.4703 g cm^{-3}, and is soluble in water at 310 K, a Log K_{ow} = -0.09 and acidity constants equal to pK_{a1} = 2.0 and pK_{a2} = 6.4. SMX has a melting point between 439 and 442 K, a Log K_{ow} = 0.89, a pK_{a1} = 1.6, and a pK_{a2} = 5.7 (Santos et al., 2011). Both are ionizable molecules and, according to the United Nations (UN), they are substances that pose a risk to the environment. Both SDZ and SMX were purchased from Sigma-Aldrich in their pure form or analytical standard.

Sorption kinetics of SDZ and SMX

Sorption kinetics were evaluated at a concentration of 10^{-4} M for both SDZ and SMX compounds. The ratios used were: soil-solution of 1:10 (5 g of soil for 50 ml of antibiotic solution in question) and biochar-soil-solution of 1:20:200 (0.25 g of biochar for 5 g of soil and 50 ml of antibiotic solution).

The amber glass bottles, 50 ml each, were placed on a shaking table at 200 rpm and the aqueous solutions were removed at times 0; 0.5; 1; 2; 3; 4; 5; 6; 8; 10; 12; 24; 36; 48; 60 and 72 h and 2 ml aliquots were collected. After shaking, the supernatant was filtered using a 0.22 µm PVDF filter (polyvinylidene fluoride) and a cellulose acetate filter membrane with 0.45 µm porosity and then centrifuged at 10,000 rpm for 10 min. This entire process was carried out in triplicate.

Antibiotic supernatant concentrations were determined by high-performance liquid chromatography (HPLC) using a Waters chromatograph, model ArcHPLC, with a diode array detector (PDA-2998) and a 150 mm XSlect (Waters) C18 column long, 4.6 mm in diameter and 5 µm thick stationary phase film.

The mobile phase used to carry the samples containing SDZ was composed of 0.5% formic acid, 35% methanol, and 64.5% water, operating with the following chromatographic condition: Flow rate of 1 ml min^{-1} and 265 ηm as ultraviolet detection length. For SMX, the assembled mobile phase had the following composition: 60% water, 20% methanol, and 20% acetonitrile, with the pH of the water adjusted to 3 with formic acid, operating at the same flow rate as SDZ and with length 267 ηm ultraviolet detection. The injected volume of each sample was 20 µl.

Sorption isotherm of SDZ and SMX

For the sorption isotherm, the same soil-solution and biochar-soil-solution kinetic relationships were used, with the following antibiotic concentrations: 10^{-3}; $5x10^{-4}$; $3x10^{-4}$; 10^{-4};$7.5x10^{-5}$; $5x10^{-5}$; 10^{-5} M. Samples were prepared in triplicate, having been shaken for 48 h for SDZ and 24 h for SMX. Both on a shaking table at 200 rpm. The supernatant was filtered, centrifuged at 10,000 rpm for 10 minutes, and analyzed by HPLC. The amount of antibiotics absorbed was determined by Equation 1:

$$S = (C_0 - C_e).FD \qquad (1)$$

where *S* represents the amount of antibiotic sorbed by the soil or soil with biochar (mg kg^{-1}), C_0 the concentration of antibiotic in the solution placed in contact with the soil or soil with biochar (mg L^{-1}), C_e is the concentration of antibiotic in the solution after the equilibrium time (mg L^{-1}) and FD the dilution factor taking into account the solution:soil ratio (FD = 50/5 = 10).

Modeling the sorption of SDZ and SMX

The sorption process can be understood as the partition of a chemical substance between the liquid and solid phases of the soil. Sorption modeling was centered around the concept of adsorption isotherm which consisted of the relationship between the concentration of the antibiotic in solution after equilibrium (C_e) and the concentration adsorbed in the soil or soil with biochar (S). There are several models for this relationship, the most frequently used one being the linear one, Equation 2.

$$S = K_d C \tag{2}$$

Where K_d represents the distribution coefficient (L^3 M^{-1}) and depends mainly on the organic matter content. The sorption kinetics can be represented mathematically by the First and Second-order models, as shown in Equations 3 and 4, respectively:

$$\log(S_{e1} - S_t) = \log S_{e1} - \frac{k_1}{2{,}303} t \tag{3}$$

$$\frac{t}{S_t} = \frac{1}{k_s} + \frac{1}{S_{e2}} t \text{ com } k_s = k_2 S_{e2}^2 \tag{4}$$

where S_{e1} represents the sorption capacity at equilibrium (mg kg^{-1}), S_t is the sorption capacity over time (mg kg^{-1}), k_1 is the First-order sorption constant (h^{-1}), S_{e2} is the sorption capacity in equilibrium for the Second-order model (mg kg^{-1}), k_2 the Second-order sorption constant (kg mg^{-1} h^{-1}) and k_S the initial sorption (mg kg^{-1} h^{-1}).

Results and discussion

The kinetics of SAs determine the time at which sorption equilibrium is reached during batch tests. In Figure 2, there are the results of the sorption kinetics for the two antibiotics analyzed and the adjustments with the Second-order kinetic model for layers 1 (0 - 20 cm) and 2 (20 - 40 cm) of the soil with and without the addition of biochar.

The initial phase of sorption of the two contaminants by the soil and the composition between soil and biochar was similar for all cases, except for the 20 - 40 cm layer of the SDZ where the combination of soil and biochar showed a much higher sorption, reaching twice the sorption presented by soil alone.

Furthermore, it is observed that for the 0-20 cm layer, the balance between the concentration of SDZ in solution and that adsorbed in the soil without biochar was reached after 36 hours of testing, with the soil without biochar having adsorbed an amount of SDZ of 70.62 mg kg^{-1}. In cases where the bottles contained soil and biochar, the equilibrium between the concentration of SDZ in solution and that adsorbed occurred 24 hours after the start of the test, with the soil with biochar adsorbing a slightly higher amount of SDZ (73.02 mg kg^{-1}), corroborating the results found by He et al. (2019), who, when studying the adsorption capacity of the outermost layer of three soils from the intrusion of biochar made from rice straw, noted increases of up to 71% in the sorption of sulfadiazine. The initial sorption rates (k_s) for SDZ were 9.52 and 19.34 mg kg^{-1} h^{-1} for the soil without and with biochar, respectively.

For the 20 - 40 cm layer of the SDZ, the balance between this contaminant and the soil containing biochar was reached after 12 h of contact, with the soil with biochar adsorbing an amount equivalent to 102.20 mg kg^{-1}. For the soil situation without biochar, the balance between SDZ in solution and that adsorbed in the soil without the addition of biochar was also reached after 12 h of contact, but the amount adsorbed was 58.08 mg kg^{-1}, or 43.17% lower.

Regarding SMX, the initial sorption phase was similar for both cases and the two depths studied. It is observed that in the 0 - 20 cm layer, the balance between the SMX in solution and the adsorbed in the soil without biochar was obtained after 12 h of contact between the soil without biochar and the solution, with the latter adsorbing 92.34 mg kg^{-1} of SMX. For the soil with biochar, at the same depth, equilibrium was also reached after 12 h of contact, however, the soil with biochar adsorbed 123.50 mg kg^{-1} of SMX, which represents an approximate increase of 34% in sorption.

In the 20 - 40 cm layer, it was observed that the balance of SMX in solution and the adsorbed in the soil without biochar was reached after 8 h of contact, with the soil without biochar adsorbing an amount of SMX equivalent to 81.51 mg kg^{-1}. For the condition in which the soil contains biochar, this balance was also reached after 8h, but the amount adsorbed was higher, reaching 95.06 mg kg^{-1} of SMX.

Tan et al. (2022) also showed that biochar, produced from microalgae biomass (Chlamydomonas sp.), was capable of removing up to 287 mg g^{-1} of SMX present in water. Other authors such as Huang et al. (2020), showed that ground biochar was able to remove 33.4 to 83.3% of the SMX present in wastewater, depending on the pyrolysis temperature (300, 450, and 600 °C) and the organic matter used (bamboo and its bagasse). Furthermore, these authors also showed that the time elapsed from the test until reaching balance varied between 8 to 12 hours, corroborating the time in which balances were obtained in the present study. However, unlike what was observed by Bai et al. (2023) the sorption of SDZ by the combination of soil and biochar was greater than that of SMX.

The start of the sorption process is rapid, as the soil surface has a large number of sorption sites available to which pollutants can be adsorbed quickly due to Van der Waals forces, hydrogen bonds, and dipole forces (Delle, 2001; Pan, 2020;

Bai et al., 2023). Over time, the number of sorption sites on the surface of the particles is reduced and consequently, the force of attraction between the soil and pollutants decreases, causing sorption to be slow and continuous until reaching equilibrium (Wang et al., 2019; Rassaei, 2023).

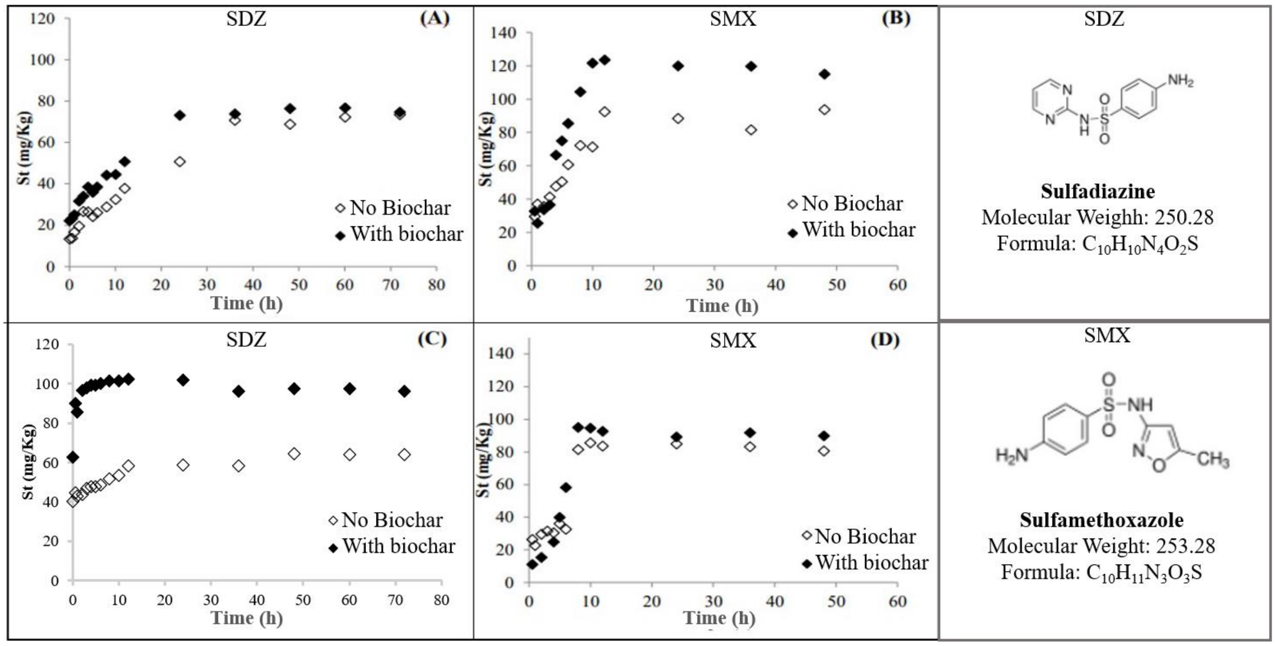

Figure 2. Sorption kinetics for the layer (A) 0 - 20 cm (SDZ), (B) 0 - 20 cm (SMX), (C) 20 - 40 cm (SDZ) and 20 - 40 cm (SMX).

Similarly, for biochar, the beginning of the adsorption process occurs quickly due to the abundance of active sites in the BC molecules. Over time, adsorption tends to become slower until it reaches equilibrium due to the decrease in free adsorption sites and the increase in electrostatic repulsions between the SA molecules adsorbed by the BC and the SA molecules contained in the solution (Ren et al., 2018; Zhang et al., 2020b).

When modeling sorption kinetics, the amount of antibiotic sorbed (S_e) was greater in the surface layers of the soil with the presence of biochar, Table 1, due to the greater supply of organic matter, as stated by Thiele-Bruhn & Aust (2004) and Cui et al. (2023), who noted an improvement in the sorption of sulfonamides due to the high affinity between antibiotic molecules and organic carbon. This fact was observed for both models, first and Second-order (S_{e1} and S_{e2}).

This is also due to the fact that the 0 - 20 cm layer has a greater specific surface area due to its granulometric composition, which has more silt and clay than the lower layer (20 - 40 cm), as well as the biochar itself, which also has a high surface area (244 m^2 g^{-1}) (Dong et al., 2023; Silva, 2023).

These results of the sorption capacities of the Second-order model (S_{e2}) are similar to the data observed during the experiments, which justifies high values of the coefficient of determination for these models (R^2 above 0.9366). In the case of the first-order model, it is noted that the sorption capacities (S_{e1}) are very different from those observed experimentally, thus resulting in lower R^2, Table 1.

Furthermore, the S_{e1} values show that soil sorption is greater than that of soil added with biochar, that is, the results observed and modeled with the first order describe opposite scenarios. Thus, the observed data show an increase in sorption when biochar is present in the soil, while the values obtained with first-order modeling show that the presence of biochar reduces the sorption of SDZ and SMX in both layers (0 - 20 and 20 - 40 cm).

Therefore, the Second-order kinetic model presented a better fit to the experimental data, since the determination coefficients were greater than 0.9366, while the First-order ones were lower than the Second-order ones in all conditions analyzed (with and without biochar and in both soil layers). However, comparisons between the R^2 values for each condition showed that the determination coefficients of the Second-order model were always higher than the First-order ones, reaching a difference of up to 0.2461. This means that chemisorption was the main factor limiting the speed of the reaction, since the sorption capacity is directly related to the number of active sites present on the soil surface with and without the addition of biochar (Fernández- Calviño et al., 2015; Rath et al., 2019; Gao et al., 2023).

Table 1 – Values of equilibrium sorption capacities, S_{e1} and S_{e2}; the sorption constants, k_1 and k_2; and the coefficients of determination, R^2, for the First and Second-order models

Antibiotics	Soils	Sorption Capacity	Sorption Rate	Determination coefficient
First-order kinetics $\log(S_{e1} - S_t) = \log S_{e1} - \frac{k_1}{2,303} t$				
		S_{e1}[mg kg^{-1}]	k_1[kg mg^{-1} h^{-1}]	R^2
SDZ (0 - 20 cm)	No biochar	64.62	0.0573	0.9661
	With biochar	55.51	0.0730	0.9709
SDZ (20 - 40 cm)	No biochar	20.45	0.0440	0.9432
	With biochar	16.70	0.2536	0.8590
SMX (0 - 20 cm)	No biochar	75.98	0.7646	0.7562
	With biochar	54.16	0.6103	0.7337
SMX (20 - 40 cm)	No biochar	74.06	0.0670	0.8552
	With biochar	30.71	0.1407	0.7704
Second-order kinetics $k_s = k_2 S_{e2}^2$				
		S_{e2}[mg kg^{-1}]	k_2[kg mg^{-1} h^{-1}]	R^2
SDZ (0 - 20 cm)	No biochar	84.034	0.0011	0.9734
	With biochar	100.00	0.0010	0.9843
SDZ (20 - 40 cm)	No biochar	64.516	0.0116	0.9997
	With biochar	96.154	0.0492	0.9982
SMX (0 - 20 cm)	No biochar	96.154	0.0024	0.9879
	With biochar	128.21	0.0035	0.9798
SMX (20 - 40 cm)	No biochar	91.743	0.0025	0.9541
	With biochar	99.010	0.0031	0.9366

The study of antibiotic sorption isotherms helps to estimate the risk of contamination of groundwater. The isotherms represent the amount of contaminant (antibiotic) sorbed per unit mass of soils with and without the presence of biochar as a function of the equilibrium concentration (Bernardino et al., 2023). The observed data, arising from the tests, were adjusted using the Linear model and the distribution and determination coefficients (K_d and R^2, respectively) are present in Table 2, as well as the sorption isotherms for the two contaminants, SMX and SDZ, and the two soil layers studied in Figure 3.

The K_d, values, obtained by the linear regression model, ranged from 0.9851 to 5.8480 l kg^{-1}. He et al. (2019), when studying the adsorption of SDZ by biochar made from rice straw, obtained similar K_d values, reaching 4.07 l kg^{-1}, showing that the values obtained in the present study are following what has been evidenced by other researchers. The values of the coefficients of the determination indicate that the linear model suited the sorption of the two sulfonamides studied well, since for low concentrations of solute the isotherm tends to be linear (Delle, 2001). In the literature, there are many studies in which a linear model was used to describe the sorption of sulfonamides (Gao & Pedersen, 2010; Yang et al., 2011; Doretto & Rath, 2013; Zheng et al., 2013; Conde-Cid et al., 2020) and for these cases, the K_d values were relevant in representing the sorption of these contaminants.

Table 2 – Distribution coefficients (K_d) of linear sorption isotherms

Antibiotic and layer	Soil	K_d [l kg^{-1}]	Determination coefficient (R^2)
SDZ (0 - 20 cm)	No biochar	3.7650	0.9883
	With biochar	0.9851	0.8261
SDZ (20 - 40 cm)	No biochar	5.8480	0.9795
	With biochar	1.0071	0.6809
SMX (0 - 20 cm)	No biochar	1.5133	0.9825
	With biochar	2.1572	0.9779
SMX (20 - 40 cm)	No biochar	1.3064	0.9467
	Com biochar	3,0008	0,9951

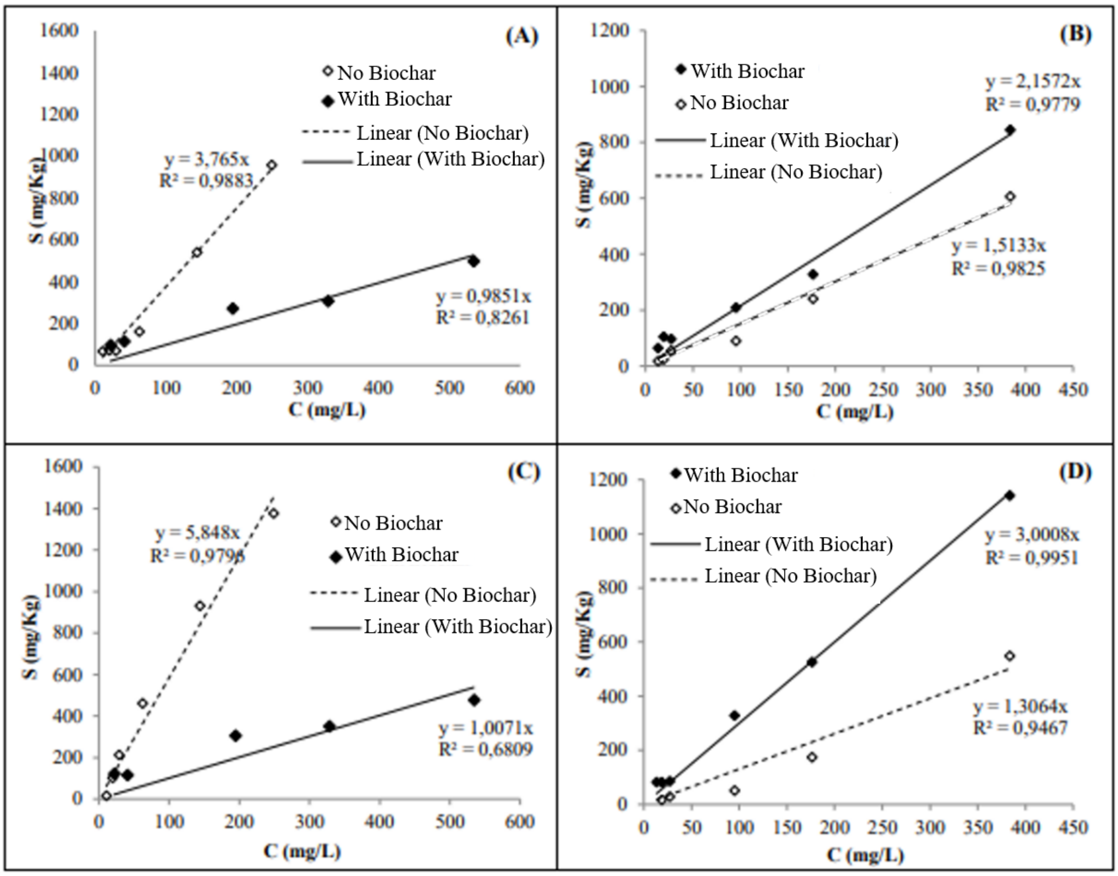

Figure 3. Sorption isotherm of sulfadiazine and sulfamethoxazole for the soil layers studied: (A) 0 - 20 cm (SDZ), (B) 0 - 20 cm (SMX), (C) 20 - 40 cm (SDZ), and (D) 20 - 40 cm (SMX).

Sorption as a function of pH

The aromatic rings of sulfonamides become strong electron acceptors due to electron withdrawal by the sulfonamide group of the molecule (Peiris et al., 2017). Amino functional groups can donate a pair of electrons from the Nitrogen atom to the aromatic rings, also behaving as electron acceptors (Ahmed et al., 2017). This ability to accept electrons by sulfonamides becomes even stronger at low pH values, due to the protonation of the amine groups and the N-heteroaromatic ring (Wijnja, Pignatello & Malekani, 2004).

Sulfadiazine and sulfamethoxazole molecules have amine groups that are ionizable in aqueous solution, when there are variations in pH, and can be configured into species with positive, neutral, and negative charges (He et al., 2019; Zhao et al., 2022). According to Peiris et al. (2017), distribution coefficients and adsorption capacities vary significantly when pH changes occur. Under natural pH conditions, sulfonamides have an acidic character and with a decrease in pH values, there is an increase in Kd values due to the neutralization of their molecules (Thiele-Bruhn & Aust, 2004).

For SMX, the greatest sorption occurred when the solution had a neutral pH, for values between three and four. The sorption potential was higher for the soil with biochar, being 195.61 mg kg^{-1} for the 0 - 20 cm layer and 187.75 mg kg^{-1} for the 20 - 40 cm layer, with a pH of 3.73. For the soil without biochar, the sorption was 141.15 mg kg^{-1} in the first layer and 111.66 mg kg^{-1} in the second. The largest amount of SMX sorbed was in the 0 - 20 cm layer, which can be justified by the greater supply of organic matter on the surface, which contributes to increased sorption, due to the affinity of SMX molecules with natural carbon of organic matter and the greater contribution of fine materials (such as silt and clay), which favors the specific surface area and, consequently, a greater quantity of active sites (Isak & Xhaxhiu, 2023), as well as what occurs with the addition of biochar (Jiang et al., 2023).

Zheng et al. (2013) and Huang et al. (2020) also observed maximum sorption of SMX when the pH of the solution was between three and four, thanks to electron donor-acceptor (EDA) interactions, as when SMX is in its neutral form it presents strong electron acceptance properties due to the molecule's deficient aromatic rings (Peiris et al., 2017).

Meanwhile, Ahmed et al. (2017) and Zhao et al. (2022) observed a low sorption capacity of SMX on BC at low pH values (pH < 1.6) due to the electrostatic repulsions that occur between the positive surfaces of SMX (SMX^+) and BC. Furthermore, as the pH increases, the percentage of SMX^- also increases and, as a consequence, there is a reduction in the adsorption of the antibiotic by BC due to electrostatic repulsions between molecules with negative charges (Li et al., 2015; Zhang et al., 2020a).

Regarding SDZ, both in the first and second layers (0 - 20 and 20 - 40 cm), the greatest sorption occurred at pH values < 2.1, which is when the compound is positively charged, indicating attraction to the particles negative results from soil and/or biochar, as was also observed by He et al. (2020), where the sorption of sulfadiazine was greater at low pH values, peaking between 2.0 and 2.5. As in SMX, SDZ sorption was also greater for the soil that contained biochar, with 384.71 mg kg^{-1} for the 0 - 20 cm layer and 369.48 mg kg^{-1} for the 20 - 40 cm layer for a pH of 1.35. In the case of soil without biochar, the sorption was 271.53 mg kg^{-1} and 231.18 mg kg^{-1} or the first and second layers, respectively, Figure 4.

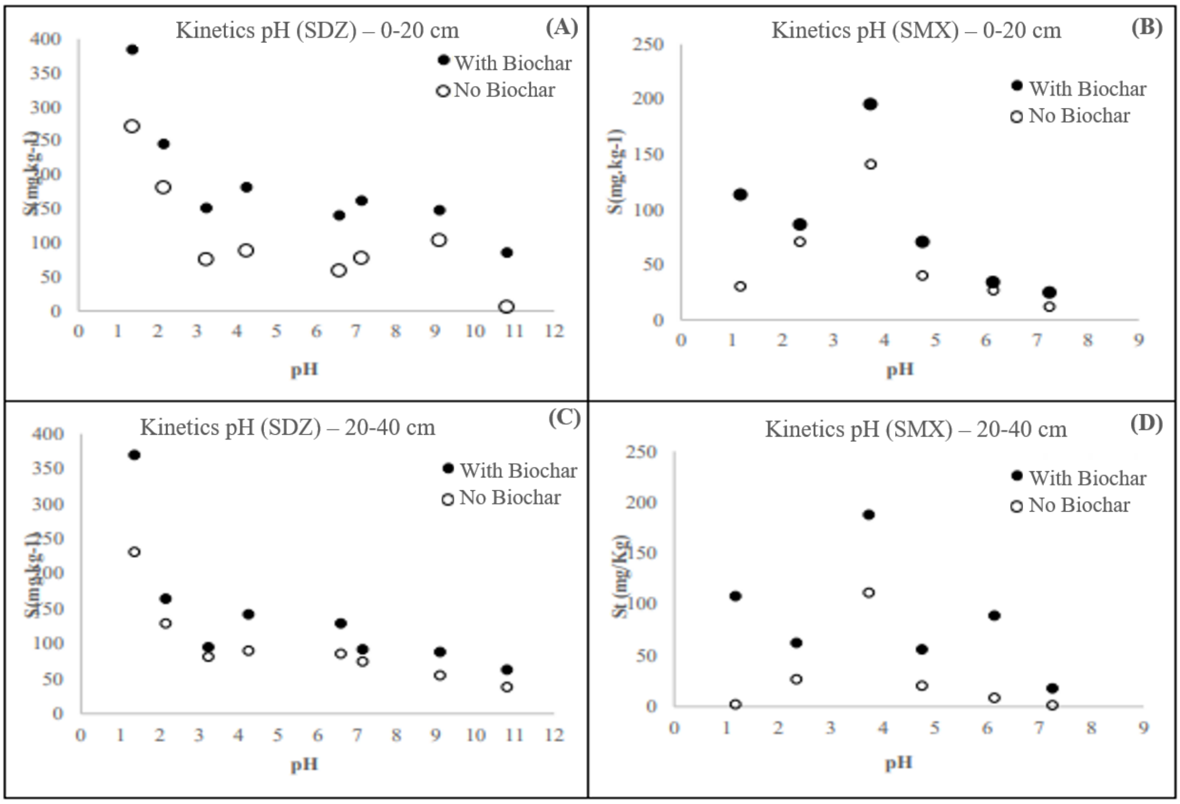

Figure 4. Sorption as a function of pH for (A) 0 - 20 cm (SDZ), (B) 0 - 20 cm (SMX), (C) 20 - 40 cm (SDZ) and 20 - 40 cm (SMX).

The fact that the amount of SDZ sorbed was greater for the 0 - 20 cm layer is also justified by the supply of organic matter on the surface, since it generally contains negative charges linked to carboxylic and phenolic functional groups, which favor the removal of pharmaceuticals in the soil (Park et al., 2018). Comparing the two antibiotics, sorption to SDZ was higher compared to SMX for all soil layers, probably due to greater acceptance of electrons by the positively charged molecules of SDZ than the neutral species of SMX.

Furthermore, for pH values close to neutral, the sorption of SDZ was approximately six times greater than that of SMX, this is because for pH = 6.8 ± 0.2 more than 94% of SMX molecules present negative charges, while that those from SDZ are neutral (Zhang et al., 2020b), with neutral molecules being more easily absorbed by biochar than negatively charged (Lian et al., 2015).

Conclusion

Knowing the sorption of sulfadiazine and sulfamethoxazole in the soil with and without the presence of biochar is of great importance to determine the potential mobility and retention of these antibiotics in the soil to estimate the potential risk of contamination of groundwater.

For the studied soil profile, equilibrium was reached after 36 and 24 hours of interaction between the SDZ and the soil in the 0 - 20 cm layer without and with biochar, while for the second layer, equilibrium was reached after 12 hours of interaction in both cases. Regarding SMX, equilibrium was reached after 12 hours of interaction between SMX and the soil in the first layer without and with biochar, and in the second layer (20 - 40 cm) the time was 8 hours. The Second-order kinetics model was the most appropriate to represent the sorption of the two antibiotics in all soil layers without and with the presence of biochar.

For the sorption isotherms, the linear model was well suited, with distribution coefficients ranging from 0.9851 to 5.8480 l Kg^{-1}, with adequate R^2 values.

The sorption of antibiotics in the soil and the soil with biochar was greatly influenced by the pH variation, with maximum sorption of SMX with pH values between three and four and SDZ with values below 2,1. Furthermore, the low values of sorption coefficients found indicate the high mobility of these antibiotics, with a risk of contamination of surface and groundwater.

Acknowledgment

This work was carried out with the support of the Coordination for the Improvement of Higher Education Personnel - Brazil - (CAPES) – Process: 888.159187/2017-01 and Financing Code 001.

References

Ahmad, M., Rajapaksha, A. U., Lim, J. E., Zhang, M., Bolan, N., Mohan, D., Vithanage. M., Lee, S. S., & Okacg, Y. S. (2014). Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere*, 99, 19–33. https://doi.org/10.1016/j.chemosphere.2013.10.071

Ahmed, M. B., Zhou, J. L., Ngo, H. H., Guo, W., Johir, M. A. H., & Sornalingam, K. (2017). Single and competitive sorption properties and mechanism of functionalized biochar for removing sulfonamide antibiotics from water. *Chemical Engineering Journal*, 311, 348–358. https://doi.org/10.1016/j.cej.2016.11.106

Bai, S., Zhou, Y., Qian, M., Xia, J., Sun, Z., Wang, Y., Huang, X., & Zhu, S. (2023). Mechanistic insights to sorptive removal of four sulfonamide antibiotics from water using magnetite-functionalized biochar. *Biochar*, 5(80), 1-12. https://doi.org/10.1007/s42773-023-00283-1

Barnes, K. K., Kolpin, D. W., Focazio, M. J., Furlong, E. T., Meyer, M. T., Zaugg, S. D., Haack, S. K., Barber, L. B., & Thurman, E. M. (2008). Water-quality data for pharmaceuticals and other organic wastewater contaminants in groundwater and in untreated drinking water sources in the United States, 2000-01. *Open File Report United State Geological Survey*, 2008(1293), 1-7.

Beesley, L., & Marmiroli, M. (2011). The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar. *Environmental Pollution*, 159(2), 474–480. https://doi.org/10.1016/j.envpol.2010.10.016

Bernardino, C. A. R., Mahler, C. F., Fernandes, J. O., Lopes, C. S. C. L., Braz, B. F., Archanjo, B. S., Santelli, R. E., & Cincotto, F. H. (2023). Evaluation of microplastic contamination by metals in a controlled environment: A risk to be considered. *Environmental Monitoring and Assessment*, 195(691), 1-14. http://doi.org/10.1007/s10661-023-11389-1

Bousdra, T., Papadimou, S. G., & Golia, E. E. (2023). The Use of biochar in the Remediation of Pb, Cd, and Cu-Contaminated Soils. The Impact of biochar Feedstock and Preparation Conditions on Its Remediation Capacity. *Land*, 12(2), 1-20. https://doi.org/10.3390/land12020383

Blenis, N., Hue, N., Maaz, T. M., & Kantar, M. (2023). Biochar Production, Modification, and Its Uses in Soil Remediation: A Review. *Sustainability*, 15(4), 1-15. https://doi.org/10.3390/su15043442

Brassard, P., Godbout, S., & Raghavan, V. (2016). Soil biochar amendment as a climate change mitigation tool: Key parameters and mechanisms involved. *Journal of Environmental Management*, 181, 484-497. https://doi.org/10.1016/j.jenvman.2016.06.063

Brooks, K., Eze, J., Onalenna, O., & Rahube, T. O. (2023). Analysis of antibiotic resistance from a rural community and wastewater contaminated environment linked to human and animal activities. *Journal of Hazardous Materials Advances*, 9, 1-12. https://doi.org/10.1016/j.hazadv.2023.100232

Budania, R., & Dangayach, S. (2023). A comprehensive review on permeable reactive barrier for the remediation of groundwater contamination. *Journal of Environmental Management*, 332, 1-10. https://doi.org/10.1016/j.jenvman.2023.117343

Brassard, P., Godbout, S., & Raghavan, V. (2016). Soil biochar amendment as a climate change mitigation tool: Key parameters and mechanisms involved. *Journal of Environmental Management*, 181, 484-497. https://doi.org/10.1016/j.jenvman.2016.06.063

Carvalho, I. T., & Santos, L. (2016). Antibiotics in the aquatic environments: A review of the European scenario. *Environment International*, 94, 736–757. https://doi.org/10.1016/j.envint.2016.06.025

Calviño, F., Couso, A. B., Estévez, M. A., Muñoz, J. C. N., Sanjurjo, M. J. F., Rodríguez, E. A., & Delga, A. N. (2015). Competitive adsorption/desorption of tetracycline, oxytetracycline and chlortetracycline on two acid soils: Stirred flow chamber experiments. *Chemosphere*, 134, 361–366. https://doi.org/10.1016/j.chemosphere.2015.04.098

Cheng, J., Lee, X., Tang, Y., & Zhang, Q. (2019). Long-term effects of biochar amendment on rhizosphere and bulk soil microbial communities in a karst region, southwest China. *Applied Soil Ecology*, 140, 126-134. https://doi.org/10.1016/j.geoderma.2022.116250

Cid, M. C., Coelho, G. F., Calviño, D. F., Delgado, A. N., Sanjurjo, M. J. F., Estévez, M. A., & Rodríguez, E. A. (2020). Single and simultaneous adsorption of three sulfonamides in agricultural soils: Effects of pH and organic matter content. Science of the Total Environment, 744, 1–14. https://doi.org/10.1016/j.scitotenv.2020.140872

Chaves, M. T. (2023). O agroturismo como instrumento de desenvolvimento e inovação: um estudo de caso na cidade de Garanhuns-PE. Dissertação (Mestrado) apresendtada ao Programa de Pós- Graduação em Gestão, Inovação e Consumo, da Universidade Federal de Pernambuco, Caruaru, PE.

Chen, Y., Li, M., Gao, W., Guan, Y., Hao, Z., & Liu, J. (2023). Occurrence and risks of pharmaceuticals, personal care products, and endocrine-disrupting compounds in Chinese surface waters. *Journal of Environmental Sciences*, 143, 1-13. https://doi.org/10.1016/j.jes.2023.10.011

Cui, S., Qi, Y., Zhu, Q., Wang, C., & Sun, H. (2023). A review of the influence of soil minerals and organic matter on the migration and transformation of sulfonamides. *Science of the Total Environment*, 861, 1-12. https://doi.org/10.1016/j.scitotenv.2022.160584

Delle, A. (2001). Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review. *Journal of Physical and Chemical Reference Data*, 30(1), 187–439. https://doi.org/10.1063/1.1347984

Empresa Brasileira de Pesquisa Agropecuária - EMBRAPA (2018, 23 de março). *Contaminantes emergentes podem ser uma ameaça na água para consumo humano*. https://www.embrapa.br/busca-de-noticias/-/noticia/32796742/contaminantes-emergentes-podem-ser-uma-ameaca-na-agua-para-consumo-humano

Dong, M., He, L., Jiang, M., Zhu, Y., Wang, J., Gustave, W., Wang, S., Deng, Y., Zhang, X., & Wang, Z. (2023). Biochar for the Removal of Emerging Pollutants from Aquatic Systems: A Review. *International Journal of Environmental Research and Public Health*, 20(3), 1-18. https://doi.org/10.3390/ijerph20031679

Dong, P., Qiu, W., He, X., Zhang, Y., & Zheng, C. (2021). Analysis of physicochemical factors regulating transport behaviors of sulfonamide antibiotics in saturated porous media. *Journal of Hydrology*, 559, 1-10. https://doi.org/10.1016/j.jhydrol.2021.126381

Doretto, K. M., & Rath, S. (2013). Sorption of sulfadiazine on Brazilian soils. *Chemosphere*, 90(6), 2027–2034. https://doi.org/10.1016/j.chemosphere.2012.10.084

Du, L., & Liu, W. (2012). Occurrence, fate, and ecotoxicity of antibiotics in agro-ecosystems. A review. *Agronomy for Sustainable Development*, 32(2), 309–327. http://doi.org/10.1007/s13593-011-0062-9

Gao, J., & Pedersen, J. A. (2010). Sorption of Sulfonamide Antimicrobial Agents to Humic Acid-Clay Complexes. *Journal of Environmental Quality*, 39(1), 228–235. https://doi.org/10.2134/jeq2008.0274

Gao, W., He, W., Zhang, J., Chen, Y., Zhang, Z., Yang, Y., & He, Z. (2023). Effects of biochar-based materials on nickel adsorption and bioavailability in soil. *Scientific Reports*, 13, 1-16. http://doi.org/10.1038/s41598-023-32502-x.

Gomes, S. C., Zhou, J. L., Zeng, Z., & Long, G. (2022). Water treatment sludge conversion to biochar as cementitious material in cement composite. *Journal of Environmental Management*, 306, 1-9. https://doi.org/10.1016/j.jenvman.2022.114463

Gong, Z., Wang, H., Vayenas, D. V., & Yan, G. (2022). Enhanced electrochemical removal of sulfadiazine using stainless steel electrode coated with activated algal biochar. *Journal of Environmental Management*, 306, 1-10. https://doi.org/10.1016/j.jenvman.2022.114535

González-Acevedo, Z. I., García-Zarate, M. A., & Flores-Lugo, I. P. (2019). Emerging contaminants and nutrients in a saline aquifer of a complex environment. *Environmental Pollution*, 244, 885–897. https://doi.org/10.1016/j.envpol.2018.10.104

Guo, X. L., Zhu, Z. W., & Li, H. L. (2014). Biodegradation of sulfamethoxazole by Phanerochaete chrysosporium, *Journal of molecular liquids*, 198, 169–172. http://dx.doi.org/10.1016/j.molliq.2014.06.017

Gupt, C. B., Kushwaha, A., Prakash, A., Chandra, A., Goswami, L., & Sekharan, S. (2020). Mitigation of Groundwater Pollution: Heavy

Metal Retention Characteristics of Fly Ash Based Liner Materials. *Microorganisms for Sustainability*, 24, 79-104. https://doi.org/10.1007/978-981-15-6564-9_5

Hansen, V., Müller-St¨Over, D., Ahrenfeldt, J., Holm, J. K., Henriksen, U. B., & Hauggaard-Nielsen, H. (2015). Gasification biochar as a valuable by-product for carbon sequestration and soil amendment. *Biomass Bioenergy*, 72, 300–308. https://doi.org/10.1016/j.biombioe.2014.10.013

He, Y., Yao, T., Tan, S., Yu, B., Liu, K., Hu, L., Luo, K., Liu, M., Liu, X., & Bai, L. (2019). Effects of pH and gallic acid on the adsorption of two ionizable organic contaminants to rice straw-derived biochar-amended soils. *Ecotoxicology and Environmental Safety*, 184, 1–7. https://doi.org/10.1016/j.ecoenv.2019.109656

Hu, X., Zhou, Q., & Luo, Y. (2010). Occurrence and source analysis of typical veterinary antibiotics in manure, soil, vegetables and groundwater from organic vegetable bases, northern China. *Environmental Pollution*, 158(9), 2992–2998. http://doi.org/10.1016/j.envpol.2010.05.023

Huang, J., Zimmerman, A. R., Chen, H., & Gao, B. (2020). Ball milled biochar effectively removes sulfamethoxazole and sulfapyridine antibiotics from water and wastewater. *Environmental Pollution*, 258, 1-7. http://doi.org/10.1016/j.envpol.2019.113809

Ibekwe, A. M., Bhattacharjee, A. S., Phan, D., Ashworth, D., Schmidt, M. P., Murinda, S. E., Obayiuwana, A., Murry, M. A., Schwartz, G., Lundquist, T., Ma, J., Karathia, H., Fanelli, B., Hasan, N. A., & Yang, C-H. (2023). Potential reservoirs of antimicrobial resistance in livestock waste and treated wastewater that can be disseminated to agricultural land. *Science of the Total Environment*, 872, 1-25. http://doi.org/10.1016/j.scitotenv.2023.162194

Isak, N., & Xhaxhiu, K. (2023). A review on the adsorption of diuron, carbaryl, and alachlor using natural and activated clays. *Remediation*, 33(4), 339-353. https://doi.org/10.1002/rem.21757

Jiang, M. He, L., Niazi, N. N., Wang, H., Gustave, W., Vithanage, M., Geng, K., Shang, H., Zhang, X., & Wang, Z. Nanobiochar for the remediation of contaminated soil and water: challenges and opportunities. *Biochar*, 5(2), 1-21. https://doi.org/10.1007/s42773-022-00201-x

Juela, D., Vera, M., Cruzat, C., Alvarez, X., & Vanegas, E. (2021). Adsorption properties of sugarcane bagasse and corn cob for the sulfamethoxazole removal in a fixed-bed column. *Sustainable Environment Research*, 31(37), 1–14. https://doi.org/10.1186/s42834-021-00102-x

Khan, S., Chao, C., Waqas, M., Arp, H. P. H., & Zhu, Y-G. (2013). Sewage Sludge Biochar Influence upon Rice (Oryza sativa L) Yield, Metal Bioaccumulation and Greenhouse Gas Emissions from Acidic Paddy Soil. *Environmental Science & Technology*, 175, 64-68. https:// dx.doi.org/10.1021/es400554x

Kümmerer, K. (2009). Antibiotics in the aquatic environment - A review - Part I. *Chemosphere*, 75(4), 417–434. https://doi.org/10.1016/j.chemosphere.2008.11.086

Kwon, S. I., Owens. G., Ok, Y. S., Lee, D. B., Jeon, W.-T., Kim, J. G., & Kim, K. -R. (2011). Applicability of the Charm II system for monitoring antibiotic residues in manure-based composts. *Waste Management*, 31(1), 39–44. http://doi.org/10.1016/j.wasman.2010.08.018

Lap, B. Q., Thinh, N. V. D., Hung, N. T. Q., Nam, N. H., Dang, H. T. T., Ba, H. T., Ky, N. M., & Tuan, H. N. A. (2021). Assessment of Rice Straw–Derived Biochar for Livestock Wastewater Treatment. *Water, Air, and Soil Pollution*, 232(4), p. 1-13. https://link.springer.com/article/10.1007/s11270-021-05100-8

Li, S., Ondon, B. S., Ho, S-H., & Li, F. (2023). Emerging soil contamination of antibiotics resistance bacteria (ARB) carrying genes (ARGs): New challenges for soil remediation and conservation. *Environmental Research*, 219, 1-11. http://doi.org/10.1016/j.envres.2022.115132

Li, T., Han, X., Liang, C., Shohag, M. J. I., & Yang, X. (2015). Sorption of sulphamethoxazole by the biochars derived from rice straw and alligator flag. *Environmental Technology (United Kingdom)*, 36(2), 245–253.

Lian, F., Sun, B., Chen, X., Zhu, L., Liu, Z., & Xing, B. (2015). Effect of humic acid (HA) on sulfonamide sorption by biochars. *Environmental Pollution*, 204, 306–312. https://doi.org/10.1016/j.envpol.2015.05.030

Lyu, J., Yang, L., Zhang, L., Ye, B., & Wang, L. Antibiotics in soil and water in China–a systematic review and source analysis. *Environmental Pollution*, 226, 2020. https://doi.org/10.1016/j.envpol.2020.115147

Martínez-Carballo, E., González-Barreiro, C., Scharf, S., & Gans, O. (2007). Environmental monitoring study of selected veterinary antibiotics in animal manure and soils in Austria. *Environmental Pollution*, 148, 570-579. http://doi.org/10.1016/j.envpol.2006.11.035

Naidu, R., & Birke, V. (2015). Permeable Reactive Barrier: Sustainable Groundwater Remediation. 1. ed. CRC Press: Taylor & Francis Group.

Nguyen, T. B., Nguyen, V., Hoang, H. G., Cao, N. D. T., Nguyen, T. T., Vo, T. D. H., Nguyen, N. K. Q., Pham, M. D. T., Nghiem, D. L., Vo, T. K. Q., Dong, C. D., & Bui, X. T. (2023). Recent development of algal biochar for contaminant remediation and energy application: a state-of-the art review. *Current Pollution Reports*, 9(1), 73–89.

Pan, M. (2020). Biochar Adsorption of Antibiotics and its Implications to Remediation of Contaminated Soil. Water Air Soil Pollution, 231(221), 1-15.

Pandit, N. R., Mulder, J., Hale, S. E., Martinsen, V., Schmidt, H. P., & Cornelissen, G. (2018). Biochar improves maize growth by alleviation of nutrient stress in a moderately acidic low-input Nepalese soil. *Science of the Total Environment*, 625, 1380–1389. https://doi.org/10.1016/j.scitotenv.2018.01.022

Park, J., Cho, K. H., Lee, E., Lee, S., & Cho, J. (2018). Sorption of pharmaceuticals to soil organic matter in a constructed wetland by electrostatic interaction. *Science of The Total Environment*, 635, 1345-1350. https://doi.org/10.1016/j.scitotenv.2018.04.212

Peiris, C., Gunatilakea, S. R., Mlsna, T. E., Mohan, D., & Vithanage, M. (2017). Biochar based removal of antibiotic sulfonamides and tetracyclines in aquatic environments: A critical review. *Bioresource Technology*, 246, 150–159. https://doi.org/10.1016/j.biortech.2017.07.150

Pradhan, B., Chand, Sujata., Chand, S., Rout, P. R., & Naik, S. K. (2023). Emerging groundwater contaminants: A comprehensive review on their health hazards and remediation technologies. *Groundwater for Sustainable Development*, 20, 1-16. https://doi.org/10.1016/j.gsd.2022.100868

Qi, J., Yang, Hua., Wang, X., Zhu, H., Wang, Z., Zhao, C., Li, B., & Liu, Z. (2023). State-of-the-art on animal manure pollution control and resource utilization. *Journal of Environmental Chemical Engineering*. 11(5), 1-26. https://doi.org/10.1016/j.jece.2023.110462

Rassaei, F. (2023). Kinetics, isotherms, thermodynamic adsorption, and desorption studies of chromium in two types of calcareous soils. *Arabian Journal of Geosciences*, 16(214), 1-11. http://doi.org/10.1007/s12517-023-11291-7

Rath, S., Fostier, A. H., Pereira, L. A., Dioniso, A. C., Ferreira, F. O., Doretto, K. M., Peruchi, L. M., Viera, A., Neto, O. F. O., Bosco, S. M. D., & Mejía, M. J. M. (2019). Sorption behaviors of antimicrobial and antiparasitic veterinary drugs on subtropical soils. *Chemosphere*, 214, 111–122. https://doi.org/10.1016/j.chemosphere.2018.09.083

Ren, X., Sun, H., Wang, F., Zhang, P., Zhu, H. (2018). Effect of aging in field soil on biochar's properties and its sorption capacity. *Environmental Pollution*, 242, 1880-1886. https://doi.org/10.1016/j.chemosphere.2021.133427

Rodriguez-Mozaz, S., Chamorro, S., Marti, E., Huerta, B., Gros, M., Sànchez-Melsió, A., Borrego, C. M., Barceló, D., & Balcázar, J. L. (2015). Occurrence of antibiotics and antibiotic resistance genes in hospital and urban wastewaters and their impact on the receiving river. *Water Research*, 69, 234–242. http://doi.org/10.1016/j.watres.2014.11.021

Sen, U., Esteves, B., Aguiar, T., & Pereira, H. Removal of Antibiotics by Biochars: A Critical Review. Applied Sciences, 13(21), p. 11963, 2023. https://doi.org/10.3390/app132111963

Siipola, P., Pflugmacher, S., Romar, H., Koukkari, L., & Koukkari, P. (2020). Low-Cost Biochar Adsorbents for Water Purification Including Microplastics Removal. *Applied Sciences*, 10(3), 1-18.

Silva, J. B. (2023). Efeito da aplicação do biochar na retenção e mobilidade do corante vermelho drimaren num solo aluvionar do alto do Capibaribe. Dissertação (Mestrado) apresendtada ao Programa de Pós-Graduação em Engenharia Civil e Ambiental, da Universidade Federal de Pernambuco.

Silva, S. S., Oliveira, M. C., Campos, J. M. S., Silva, J. L., Moreira, G. R., Monteiro, C. C. F., Moraes, G. S. O., & Ferreira, M. A. (2019). Viabilidade econômica em sistemas de produção de leite da Agricultura familiar em Pernambuco. *Custos e Agronegócio Online*, 15(3), 460– 483.

Spielmeyer, A., Petri, M. S., Höper, H., & Hamscher, G. (2020). Long-term monitoring of sulfonamides and tetracyclines in manure amended soils and leachate samples - A follow-up study. *Heliyon*, 6(8). https://doi.org/10.1016/j.heliyon.2020.e04656

Tan, X., Wei, H., Zhou, Y., Zhang, C., & Ho, S. (2022). Adsorption of sulfamethoxazole via biochar: The key role of characteristic components derived from different growth stage of microalgae. *Environmental Research*, 210, 1-7. https://doi.org/10.1016/j.envres.2022.112965

Thiele-Bruhn, S., & Aust, M. O. (2004). Effects of pig slurry on the sorption of sulfonamide antibiotics in Soil. *Archives of Environmental Contamination and Toxicology*, 49(1), 31-39. http://doi.org/10.1007/s00244-003-3120-8

Vithanage, M., Rajapaksha, A. U., Zhang, M., Thiele-Bruhn, S., Lee, S. S., OK, Y. S. (2015). Acid-activated biochar increased sulfamethazine retention in soils. *Environmental Science and Pollution Research*, 22, 2175-2186.

Wang, B., Zeng, D., Chen, Y., Belzile, N., Bai, Y., Zhu, J., Shu, J., & Chen, S. (2019). Adsorption behaviors of phenanthrene and bisphenol A in purple paddy soils amended with straw-derived DOM in the West Sichuan Plain of China. *Ecotoxicology and Environmental Safety*, 169, 737–746. https://doi.org/10.1016/j.ecoenv.2018.11.096

Wijnja, H., Pignatello, J. J., & Malekani, K. (2004). Formation of π-π Complexes between Phenanthrene and Model π-Acceptor Humic Subunits. *Journal of Environmental Quality*, 33(1), 265–275. http://doi.org/10.2134/jeq2004.2650

Yan, C., Yang, Y., Zhou, J., Liu, M., Nie, M., Shi, H., & Gu, L. (2013). Antibiotics in the surface water of the Yangtze Estuary: Occurrence, distribution and risk assessment. *Environmental Pollution*, 175, 22–29. https://doi.org/10.1016/j.envpol.2012.12.008

Yang, S. F., Lin, C. F., Angelayu-Chen Lin, A. Y. C., & Hong, P. K. A. (2011). Sorption and biodegradation of sulfonamide antibiotics by activated sludge: Experimental assessment using batch data obtained under aerobic conditions. *Water Research*, 45(11), 3389–3397. https://doi.org/10.1016/j.watres.2011.03.052

Zhang, C., Chen, Y., Chen, S., Guan, X., Zhong, Y., & Yang, Q. (2023). Occurrence, risk assessment, and in vitro and in vivo toxicity of antibiotics in surface water in China. *Ecotoxicology and Environmental Safety*, 255, 1-12. https://doi.org/10.1016/j.ecoenv.2023.114817

Zhang, M., He, L. Y., Liu, Y. S., Zhao, J. L., Liu, W. R., Zhang, J. N., Chen, J., He, L. K., Zhang, Q. Q., & Ying, G. G. (2019). Fate of veterinary antibiotics during animal manure composting. *Science of the Total Environment*, 650, 1363–1370. https://doi.org/10.1016/j.scitotenv.2018.09.147

Zhang, R., Xiaoxian Zheng, X., Chen, B., Ma, J., Niu, X., Zhang, D., Lin, Z., Fu, M., & Zhoua, S. (2020a). Enhanced adsorption of sulfamethoxazole from aqueous solution by Fe-impregnated graphited biochar. *Journal of Cleaner Production*, 256, 1-12. https://doi.org/10.1016/j.jclepro.2020.120662

Zhang, X., Zhang, Y., Ngo, H. H., Guo, W., Wen, H., Zhang, D., Li, C., & Qi, L. (2020b). Characterization and sulfonamide antibiotics adsorption capacity of spent coffee grounds based biochar and hydrochar. *Science of the Total Environment*, 716, 2020b. https://doi.org/10.1016/j.scitotenv.2020.137015

Zhang, Y., Hu, S., Zhang, H., Shen, G., Yuan, Z., & Zhang, W. (2017). Degradation kinetics and mechanism of sulfadiazine and sulfamethoxazole in an agricultural soil system with manure application. *Science of the Total Environment*, 607–608, 1348–1356. http://doi.org/10.1016/j.scitotenv.2017.07.083

Zhao, Y., Zhao, C., Yang, Y., Li, Z., Qiu, X., Gao, J., & Ji, M. (2022). Adsorption of sulfamethoxazole on polypyrrole decorated volcanics over a wide pH range: Mechanisms and site energy distribution consideration. *Separation and Purification Technology*, 283, 1-12. https://doi.org/10.1016/j.seppur.2021.120165

Zheng, H., Zheng, H., Wang, Z., Zhao, J., Herbert, S., & Xing, B. (2013). Sorption of antibiotic sulfamethoxazole varies with biochars produced at different temperatures. *Environmental Pollution*, 181, 60–67. http://doi.org/10.1016/j.envpol.2013.05.056