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CARBENDAZIM ADSORPTION ON GRANULAR ACTIVATED CARBON OF COCONUT SHELL: OPTIMIZATION AND THERMODYNAMICS

* Ian Rocha de Almeida [1]
Salatiel Wohlmuth da Silva [1]
Lígia Conceição Tavares [1]
Antônio Domingues Benetti [1]

Abstract

The adsorption of the fungicide Carbendazim (CBZ) on granular activated carbon (GAC) of coconut shell was investigated through batch tests in deionized water. The most favorable conditions for the adsorption of CBZ were examined through the variation of the mass of GAC, temperature, and contact time. The Response Surface Methodology (RSM) was applied, seeking the best adsorption condition to optimize future tests. A thermodynamic analysis was carried out using the Van't Hoff method. The tests with the dosage of 10 mg of GAC and temperatures of 25º C and 30º C showed higher adsorption of the fungicide. The Freundlich isotherm adjusted best to the adsorption of the compound. The Freundlich intensity parameter had a result that contrasted with the value of ΔG regarding a spontaneous change. Physisorption predominates the adsorption of CBZ on GAC. It is an exothermic and spontaneous process that reduces the degree of disorder of the adsorbent/solution interface.

Keywords: carbendazim adsorption, granular activated carbon, adsorption optimization, response surface methodology, adsorption thermodynamics.

[1] Instituto de Pesquisas Hidráulicas, Universidade Federal do Rio Grande do Sul, Brasil.
* *Autor correspondente*: Instituto de Pesquisas Hidráulicas, Universidade Federal do Rio Grande do Sul, Avenida Bento Gonçalves, 9500 – Agronomia, Porto Alegre, Rio Grande do Sul. 91501-970. Brasil. Email: ianrochalmeida@gmail.com

Introduction

The release of contaminants from point and diffuse sources derived from human activities impacts water quality. Among the pollutants are Contaminants of Emerging Concern (CEC), which are chemical compounds present at low concentrations (usually at levels of µg/L or ng/L) in water and sewage that cause risks to human health and ecosystems (Benner *et al.*, 2013). They result from various human activities in urban areas, industry, and agriculture. Pesticides, pharmaceuticals, and flame retardants are examples of CEC that can be found in water (Kümmerer, 2011).

Interest in the study of CEC in water bodies has grown over the years, considering their impacts on aquatic ecosystems and water sources used for human consumption. Conventional water treatment processes have limitations in removing several CEC, and there is a global need to regulate the emission of most of these contaminants (Hallé *et al.*, 2015). Studies have shown that these contaminants may have deleterious effects on the environment and public health, depending on the concentration and exposure time of the organisms (Paredes *et al.*, 2016).

Among the CEC, a group that stands out is pesticides. According to the Brazilian National Health Surveillance Agency (ANVISA, 2019), pesticides are substances applied to crops, pastures, and the environment to control the action of harmful plants and insects. They are used as defoliants, desiccants, growth stimulators, and inhibitors. In recent decades, Brazil has been one of the largest consumers and producers of pesticides in the world, being the first in both aspects in Latin America (Barbosa *et al.*, 2015; Prete *et al.*, 2017; Coelho and Rozário, 2019).

One of the most applied pesticides in Brazil is Carbendazim (CBZ), the commercial name for methyl benzimidazole-2-ylcarbamate. CBZ is an agricultural defensive from the group of benzimidazoles (Rama *et al.*, 2014). It is considered a systemic fungicide with authorized application in Brazil for cotton, rice, citrus, beans, apple, corn, soybean, and wheat crops (Rama, 2013). CBZ is efficient against various fungal diseases in these crops caused by the fungi *Ascomycetes spp.*, *Basidiomycetes*, and *Deuteromycetes* spp (Coutinho *et al.*, 2007).

CBZ is used in agriculture to protect and eradicate several pathogens that affect fruits, nuts, vegetables, and other crops. Also, it can be applied in post-harvest storage and pre-planting seeds. Figure 1 shows the chemical structure of CBZ (Chemicalize, 2019). The benzimidazole ring provides resistance to molecule breakdown and slow degradation, persisting in the environment for a long time (Pourreza *et al.*, 2015).
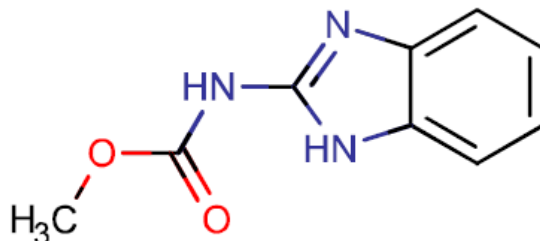
Figure 1. Chemical structure of Carbendazim (Chemicalize, 2019).

CBZ is one of Brazil's most commercialized pesticide-active ingredients (Barbosa *et al*., 2015). In 2012, the American Food and Drug Administration (FDA) detected CBZ in concentrated orange juice exported from Brazil to the United States (Yukhananov, 2012). This finding caused a decline in the application of CBZ in Brazil. In the last decade, CBZ was the main pesticide used irregularly in Brazil, being detected in unauthorized crops and above the maximum levels allowed by Brazilian legislation (Rama *et al*., 2014).

CBZ has been identified in surface waters in several countries. According to a survey carried out by Merel *et al.* (2018), CBZ was identified in water bodies in Brazil, Chile, China, Colombia, Denmark, Germany, Greece, Portugal, Romania, Serbia, Spain, and Switzerland with concentrations ranging from 10 ng/L to 6,000 ng/L. In Brazil, it is not possible to assess the population's exposure to CBZ and other pesticides due to inconsistencies in the drinking water monitoring system (Barbosa *et al*., 2015). Brazilian regulation sets an upper limit of 120 µg/L for CBZ in drinking water (Brazil, 2021).

According to Coutinho *et al*. (2007), the Pesticide Action Network (PAN, 2020), and the International Program on Chemical Safety (IPCS, 2020), CBZ is a compound that has carcinogenic potential in addition to being a possible endocrine disruptor. It is a highly toxic compound for the aquatic community: amphibians (genetic effects and mortality), aquatic plants (reproduction), crustaceans (mortality), fish (bioaccumulation and mortality), fungi (development and reproduction), mollusks (intoxication and mortality) and plankton (intoxication, growth, reproduction, and mortality).

To mitigate the impacts on the environment and human health caused by the exposure of organisms to concentrations of pesticides considered toxic, several studies have been carried out on treatment technologies to remove these compounds. Activated carbon has become one of the most used adsorbents to remove complex contaminants in aqueous solutions (Crittenden *et al*., 1987; Rathi and Kumar, 2021).

In drinking water treatment, Granular Activated Carbon (GAC) is used as an adsorbent to remove contaminants such as pesticides, drugs, and organic compounds from industrial sources, among other CEC (Kearns *et al.*, 2020). The use of GAC is justified by the relative practicality of operation and maintenance and its effectiveness compared to other treatment techniques (Joss *et al.*, 2008; Anfar *et al.*, 2020).

To optimize the removal conditions of a given compound by adsorption on activated carbon, laboratory tests are needed to identify the best operational parameters such as temperature, contact time, and mass of activated carbon used. The Response Surface Methodology (RSM) is a collection of statistical and mathematical techniques used to develop, optimize, and improve the operation of processes (Rifi *et al.*, 2022). RSM is used to assess the relative significance of factors that affect a data response (Zhou *et al.*, 2015). This methodology aims to optimize the levels of experimental variables to obtain the best system performance (Bezerra *et al.*, 2008; Rifi *et al.*, 2022).

RSM has been used to optimize and model the adsorption process to identify the best operating conditions to achieve greater efficiency in removing the compound of interest, studying the effect of parameter variation (Taktak *et al.*, 2015). The RSM is based on a multivariate nonlinear model, allowing the determination of mathematical equations with a better correspondence with the data obtained in experimental tests (Anfar *et al.*, 2020).

This research studied the removal of CBZ by adsorption on GAC in batch tests. The GAC mass, water temperature, and contact time were varied, and the best condition for CBZ removal was identified using RSM. The adjustment of the experimental data to Langmuir and Freundlich isotherms was verified. The thermodynamics of CBZ adsorption in GAC was also investigated. A literature review did not find a similar approach for CBZ adsorption on GAC from coconut shell, the adsorbent used in the experiments.

Methodology
Adsorbate and adsorbent
Adsorption tests were made using commercial GAC produced from coconut shells. Table 1 indicates the characteristics of the GAC used in the experiments. The tests were carried out with particle sizes in the range of sieves 20 × 50 mesh (0.841 x 0.297 mm). GAC was previously washed with abundant deionized water to remove fine particles, and GAC was soaked repeatedly many times. In sequence, the material was dried in an oven at a temperature of 105°C for 24 h.

Table 1. Coconut shell GAC Specifications (Teixeira, 2014; Mavaieie Júnior, 2019).

Specifications		Value
Iodine number (mg/g)		883
Ashes (%)		Max. 10
Moisture (%)		Max. 10
Apparent density (g/cm³)		0.45 – 0.55
Granulometry (Nominal, mesh)		6×10 – 6×12 - 8×16 - 12×25 – 8×30 - 12×40 – 20×50
Hardness (%)		Min. 90
Uniformity Coefficient		1.59
BET surface area (m²/g)		1,218
Pores distribution (%)	Primary Micropores (pore <0.8 nm)	54.1
	Secondary Micropores (0.8 nm < pore <2 nm)	34.5
	Mesopores (2 nm < pore <50 nm)	8.8
	Macropores (50 nm > pore)	2.6

Granular Activated Carbons manufactured from coconut shells have most of their total void volume as micropores (Crittenden *et al*., 2012). The surface area and iodine number of GAC are, respectively, in the range of 700-1,300 m^2/g and 600-1,100 mg/g (Metcalf and Eddy, 2003). The iodine number generally correlates well with the surface area available for the adsorption of small molecules (Summers *et al*., 2011; Narbaitz and McEwen, 2012). The values for ash, apparent density, and uniformity coefficient are also in the range presented by these authors.

CBZ from Sigma-Aldrich with 97% purity was used. Synthetic solutions were prepared with deionized water to a final CBZ concentration of 5.0 mg/L and neutral pH. For this research, a concentration of 5.0 mg/L was chosen. This level of concentration is not likely to be found in the environment, but it was believed it would allow better monitoring of the adsorption process and the thermodynamic data. Also, this concentration had a good fit with the curve calibration. Analyzes were performed in a Shimadzu High-Performance Liquid Chromatograph (HPLC) (LC20A) equipped with a diode array detector (DAD, SPD-20AV) and an autosampler (SIL-20A). The HPLC was operated at a 1 mL/min flow rate, and the detector was set at λ = 285 nm. The stationary phase was HyperCloneTM 5 μm ODS C18 column (4.6 mm × 100 mm, Phenomenex). The mobile phase was phosphate buffer and acetonitrile (75:25%). An injection volume of 20 μL was used. In these conditions, the CBZ retention time was 2.7 min (Machado *et al*., 2022).

The mass of GAC used in the batch tests were 0.0; 0.2; 0.5; 1.0; 1.5; 2.0; 5.0 and 10.0 mg. The tests were carried out at temperatures of 30ºC and contact times of 2h (E-1), 3h (E-2), and 4h (E-3), 25ºC (E-4, E-5, and E-6, respectively for 2, 3, and 4h), and 40ºC (E-7, E-8, and E-9, for 2, 3, and 4h). The solutions containing CBZ and GAC were stored in a Dubnoff Bath Shaker equipment, model TE-053, allowing the control of temperature and agitation. Due to restrictions on the time of access and stay at the laboratory due to the COVID-19 pandemic in Brazil, the variation of parameters was restricted to 3 different temperatures and a maximum contact time of 4 hours. All experiments were conducted in triplicate.

Adsorption Isotherms
The experimental results of CBZ adsorption on GAC were fitted to the Langmuir and Freundlich isotherms. The R² coefficients and trend lines were determined with Microsoft Office Excel (MOE) 2019 software. The Solver function was used to calculate the isotherm variables. The Langmuir and Freundlich isotherms are represented, respectively, by Equations 1 and 2 (Crittenden *et al.*, 2012).

$$q_e = q_{max} . \frac{b . C_e}{1 + b . C_e} \qquad \text{Equation (1)}$$
$$q_e = k_f . C_e^{1/n} \qquad \text{Equation (2)}$$

Where: C_e is the equilibrium concentration of adsorbate in solution after adsorption (mg/L); q_e is the quantity sorbed at equilibrium (mg/g); $q_{máx}$ is the maximum adsorption capacity (mg/g); b is the Langmuir adsorption equilibrium constant (L/mg); k_f is the Freundlich constant, representing the adsorption capacity [(mg/g) (L/mg)$^{1/n}$]; $1/n$ is the Freundlich intensity parameter. (Metcalf and Eddy, 2003; Haro *et al.*, 2021).

For comparative purposes, the linearized forms of the models were also investigated (Equations 3 and 4).

$$\frac{C_e}{q_e} = \frac{1}{b . q_{max}} + \frac{C_e}{q_{max}} \qquad \text{Equation (3)}$$
$$\ln q_e = \ln k_f + \frac{1}{n} . \ln C_e \qquad \text{Equation (4)}$$

Thermodynamic analysis
For the thermodynamic analysis, the variations in enthalpy (ΔH, kJ/mol), entropy (ΔS, J/mol.K), and Gibbs Free Energy (ΔG, kJ/mol) were quantified using equations 5 to 7 (Nekouei *et al.*, 2015; Haro *et al.*, 2021). The values of ΔH and ΔS were obtained using the Van't Hoff graph (lnKe as a function of 1/T) represented by Equation 5.

$$\ln K_e = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$ **Equation (5)**

Where: Ke is the equilibrium constant; R is the universal gas constant, 8.314 J/mol.K; and T is Temperature (K).

The adsorption equilibrium constant can be expressed by the ratio of the equilibrium concentration of the contaminant in the activated carbon to the equilibrium concentration of the contaminant in the solution expressed in Equation 6 (Mansouriieh *et al*., 2016; Prete *et al*., 2017).

$$K_e = \frac{q_e}{C_e}$$ **Equation (6)**

The variation of free energy (ΔG) was calculated with Equation 7.

$$\Delta G = -RT\ln K_e$$ **Equation (7)**

Statistical analysis
Response Surface Methodology (RSM) curves were performed for each contact time tested, totaling 3 curves. For these statistical tests, two independent variables were adopted: Y (temperature of 25° C, 30° C, and 40° C) and X (Mass of GAC from 0.0 to 10.0 mg) and a dependent variable Z (Efficiency of CBZ removal). The quadratic model was used to optimize the responses as a function of the independent variables. The application of the RSM was performed with the Statistica 13.5 software.

Statistical tests were used to check if the CBZ removal percentages had significant differences. The block design method was applied using the "Mass GAC" treatment. The "Time" and "Temperature" factors were combined to build the block variable. The variance model (ANOVA) was fitted to the data, and the F test was used to test the null hypothesis of no difference between the means. Tukey's honestly significant difference (HSD) test for multiple comparisons was used to detect which groups differed from one another. The 5% significance level was adopted in all analyses ($p = 0.05$). Boxplot graphs were created to present the distribution of the response variable (dependent variable). These analyzes were performed using R software version 4.0.4.

Results and discussion
Table 2 shows the results obtained in the adsorption experiments for the contact time, temperature, and GAC mass that were tested. The initial concentration of CBZ was 5 mg/L.

Table 2. Removal of CBZ in the adsorption tests (%).

Tests	GAC (mg)							
	0	0.2	0.4	1.0	1.5	2.0	5.0	10.0
E-1	0.0	1.1	2.8	6.5	7.5	10.5	23.2	29.8
E-2	0.0	0.4	8.6	12.1	16.7	18.1	21.8	25.7
E-3	0.0	3.5	8.7	14.9	17.9	18.8	27.7	31.6
E-4	0.0	6.5	13.8	15.3	18.7	21.3	24.3	25.4
E-5	0.0	3.5	5.9	10.1	10.7	10.7	15.6	25.8
E-6	0.0	9.5	11.0	18.7	20.3	21.1	27.0	33.3
E-7	0.0	6.7	10.4	15.2	15.8	20.5	21.5	23.5
E-8	0.0	11.3	11.6	13.8	14.9	20.4	23.0	26.0
E-9	0.0	6.7	8.7	10.1	12.7	15.8	16.6	22.3

E-1: 2 h, 30ºC; E-2: 3 h, 30ºC; E-3: 4 h, 30ºC; E-4: 2 h, 25ºC; E-5: 3 h, 25ºC; E-6: 4 h, 25ºC; E-7: 2 h, 40ºC; E-8: 3 h, 40ºC; E-9: 4 h, 40ºC;

The highest CBZ removal efficiencies occurred in tests E-3 and E-6, which presented 31.6% and 33.3%, with a contact time of 4 h, 10 mg of GAC, and temperatures of 30 ℃ and 25 ℃, respectively. Contact time and carbon mass influenced the removal efficiency of CBZ in batch tests. It is possible that the use of the higher mass of GAC and longer contact time would improve CBZ removal by adsorption. The block stratification shown in Figure 2 corroborates the best performances of CBZ ̶adsorption in tests at 25 ℃ and 30 ℃ (E-6 and E-3) and a contact time of 4h. In Figure 2, blocks include efficiencies considering all GAC masses applied in each test.
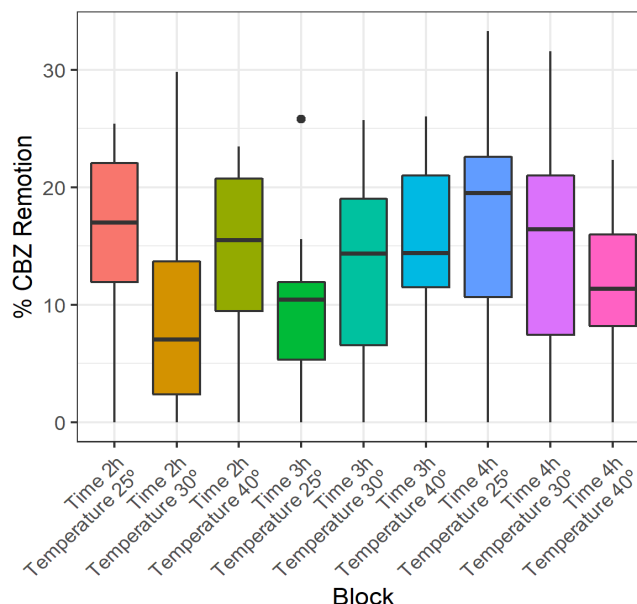
Figure 2. Distribution of stratified CBZ removal percentage by block. Each block considered efficiencies achieved by all GAC masses applied to each box.

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Figure 2 shows the highest removal efficiency at E-3 and E-6, above 30%. E-1 presented the lowest efficiency values in the second and third quartiles but showed maximum efficiency close to 30%. Only E-5 presented an outlier.

Table 3 shows the difference between the averages of CBZ removal efficiency by GAC mass, the lower and upper limits (LL and UL, respectively), and the adjusted p-value considering the 5% significance level. The approach aims to investigate whether there were significant differences between the ranges of GAC masses adopted to execute the experiments.

Table 3. Differences between treatment means (GAC mass), 95% confidence intervals (CI), and adjusted p-value (Tukey's HSD).

Breaks (mg)	Differences	LL – CI 95%	UL – CI 95%	p adjusted
0.2-0	0.0548	0.0155	0.0941	0.0012
0.5-0	0.0906	0.0514	0.1299	0.0000
1-0	0.1298	0.0905	0.1690	0.0000
1.5-0	0.1503	0.1110	0.1896	0.0000
2-0	0.1747	0.1354	0.2140	0.0000
5-0	0.2228	0.1835	0.2621	0.0000
10-0	0.2705	0.2312	0.3098	0.0000
0.5-0.2	0.0358	-0.0035	0.0751	0.0985
1-0.2	0.0749	0.0357	0.1142	0.0000
1.5-0.2	0.0955	0.0562	0.1348	0.0000
2-0.2	0.1199	0.0806	0.1592	0.0000
5-0.2	0.1680	0.1287	0.2073	0.0000
10-0.2	0.2157	0.1764	0.2550	0.0000
1-0.5	0.0391	-0.0002	0.0784	0.0517
1.5-0.5	0.0596	0.0204	0.0989	0.0003
2-0.5	0.0841	0.0448	0.1234	0.0000
5-0.5	0.1322	0.0929	0.1715	0.0000
10-0.5	0.1799	0.1406	0.2192	0.0000
1.5-1	0.0205	-0.0188	0.0598	0.7216
2-1	0.0450	0.0057	0.0843	0.0144
5-1	0.0931	0.0538	0.1324	0.0000
10-1	0.1408	0.1015	0.1800	0.0000
2-1.5	0.0244	-0.0148	0.0637	0.5177
5-1.5	0.0725	0.0333	0.1118	0.0000
10-1.5	0.1202	0.0810	0.1595	0.0000
5-2	0.0481	0.0088	0.0874	0.0068
10-2	0.0958	0.0565	0.1351	0.0000
10-5	0.0477	0.0084	0.0870	0.0075

Most of the results showed significant differences ($p < 0.05$), indicating that variations in temperature, contact time, and adsorbent mass influenced the adsorption of CBZ on GAC. However, there were no significant differences in the concentration intervals between 0.5-0.2 mg, 1.0-0.5 mg, 1.5-1.0 mg, 2.0-1.0 mg and 2.0-1.5 mg. In these ranges of GAC masses, the results showed similar behaviors.

Table 4 shows the means of CBZ removal by GAC mass. The letters "a" to "g" indicate the groupings between the treatment removals considering the significance level of 5%. It is observed that the average of CBZ removal for 10, 5, and 0 mg presented unique behaviors, and they are not grouped with other GAC masses. The other masses showed similar means of removal to the upper or lower level. That was the reason why some experiments had more than one letter ("cd", for example), representing similar behavior to the upper or lower levels.

Table 4. Averages of % removal by GAC mass.

GAC (mg)	Removal (%)	Groupings
10.0	27.05	a
5.0	22.28	b
2.0	17.47	c
1.5	15.03	cd
1.0	12.98	de
0.5	9.06	ef
0.2	5.48	f
0.0	0.00	g

Tests in which 10 mg of GAC was used presented a significant difference in the CBZ removal mean compared to all other masses ($p < 0.05$). The stratified block analysis shown in Figure 3 indicates that the assays performed by this GAC dosage showed greater fungicide removal. Likewise, the figure suggests an increase in the adsorbed concentration of CBZ, with the increase in the mass of adsorbent employed. The addition of GAC in amounts greater than 10 mg will probably result in higher CBZ removal

CBZ has constant dissociation (pKa) equal to 4.29 (PubChem, 2020). It means that if the pH of the medium is higher than the pKa, the concentration of the anionic fraction of the pesticide will be predominant, and the compound tends to be leached more easily (Barceló and Hennion, 1997). All batch adsorption tests were made with pH close to 7.0, favoring leaching and reducing adsorption.
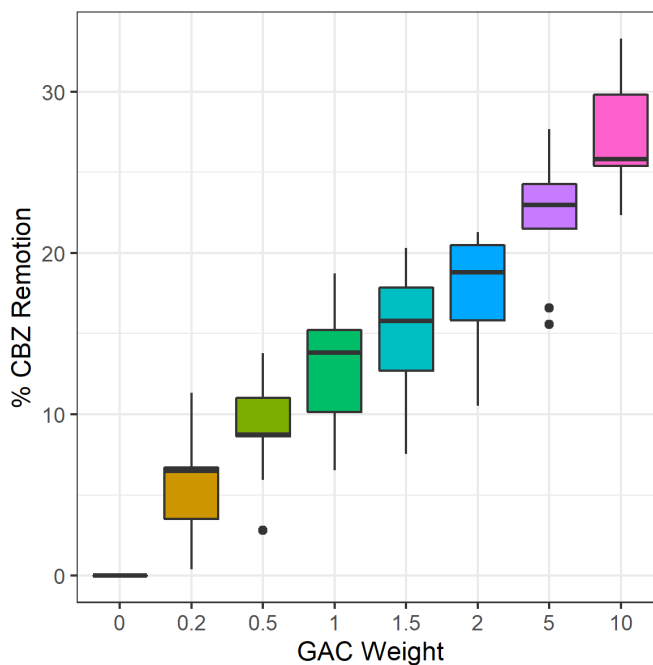
Figure 3. Distribution of CBZ removal stratified by GAC in tests.

CBZ has an octanol/water partition coefficient (log K_{ow}) and organic carbon adsorption coefficient in soil (K_{oc}) equal to 1.52 and 200 cm³/g, respectively. CBZ can be considered hydrophilic (Rogers, 1996) and moderately mobile, with a moderate tendency to sorption in the soil (Barceló and Hennion, 1997).

Surface curves relating to GAC mass, contact time, and temperature were prepared using adsorption data from Table 2. The results are shown in Figure 4.

Figure 4a shows that the curve for 2 h presents two elevations and does not provide evidence of the optimization of CBZ adsorption on the GAC. Hence, it is not possible to identify a favorable condition for removing the fungicide. This behavior occurred due to the short contact time, which might have prevented good adsorption.

Figure 4b exhibits a curve flattening with increases in temperature and GAC mass. This scenario suggests that the increase in temperature and GAC mass favors the adsorption of CBZ. However, as shown in Table 2, the fungicide removal efficiencies were not significantly different for the temperatures of 25, 30, and 40º C (p<0.05), respectively 25.8%, 25.7%, and 26.0%. Due to results that had similar behaviors, it was not possible to identify a tendency in Figure 4b.
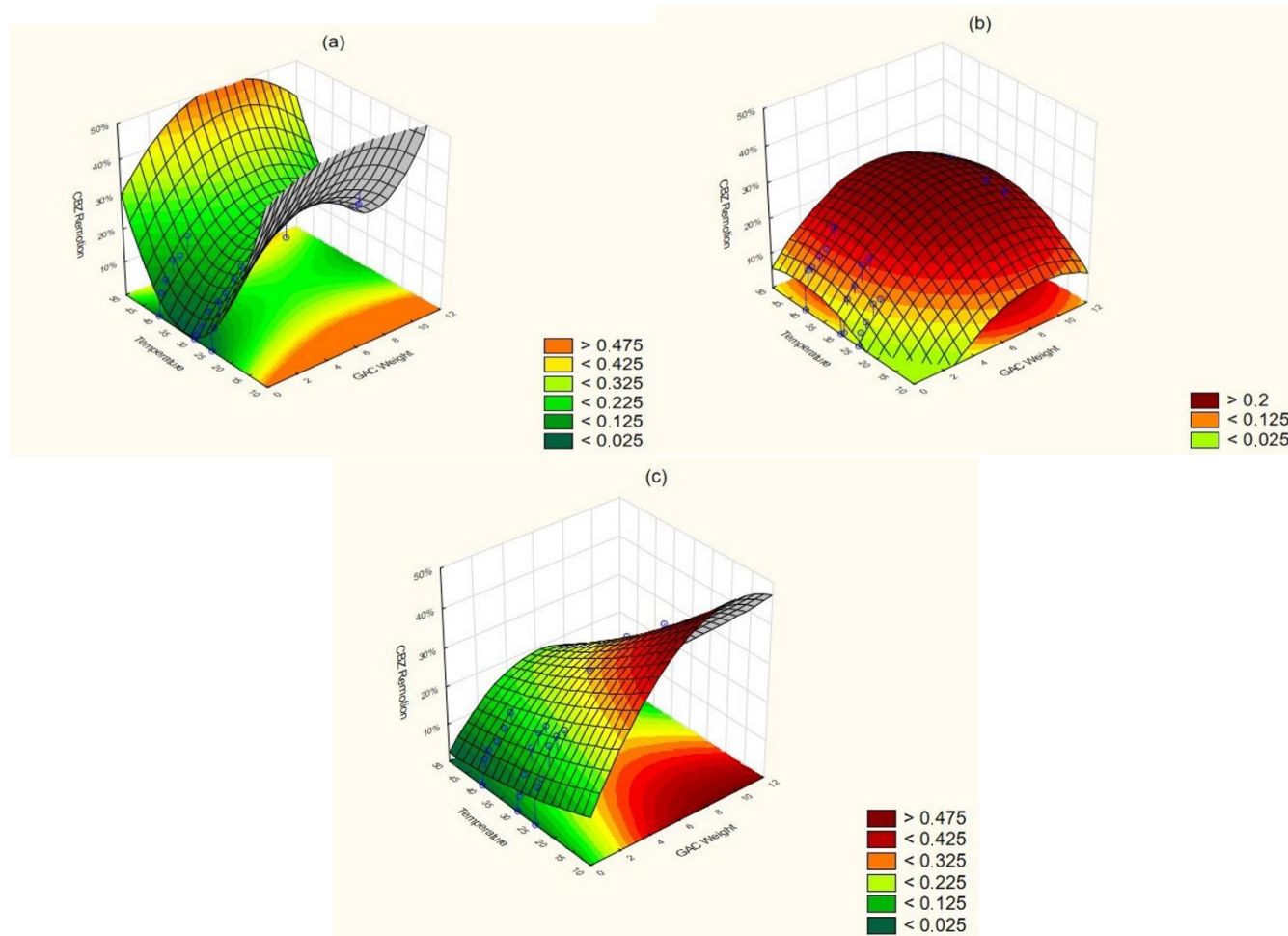
Figure 4. Surfaces curves for removal of CBZ as a function of GAC mass and temperature at 2h (a), 3h (b), and 4h (c).

In Figure 4c it is possible to observe that there is a trend in which the greatest CBZ removal occurs at the lowest temperatures associated with the highest GAC mass, with the removals of 33.3%, 31.6%, and 22.3%, respectively for the temperatures of 25° C, 30° C, and 40° C. Thus, for the contact time of 4h the adsorption of CBZ on GAC was favored at the lowest temperature (25°C), suggesting an exothermic process, as expected for adsorption (Rathi and Kumar, 2021). RSM suggests that tests could be carried out at temperatures below 30°C, reducing the number of analyzes.

Equation 8 shows the quadratic model representing Figure 4c. With this equation is possible to estimate the CBZ removal, giving temperature and GAC mass.

$$CBZ_{remotval}(\%) = 0.174 + 0.087X - 0.005Y - 0.004X^2 - 0.001XY + 4.577 \cdot 10^{-5}Y^2$$

Equation (8)

Where X is GAC mass (mg) and Y is the temperature (°C).

Table 5 shows the parameters and the correlation coefficients of the Freundlich (F) and the Langmuir (L) isotherms, determined using the linear and the nonlinear methods (Equations 1 to 4). Test E-2 (2 h, 30°C) had a poor correlation for both isotherms, and it was not further considered for analysis.

Table 5. Langmuir (L) and Freundlich (F) isotherm coefficients for each test.

Parameters			Test							
			E-1	E-3	E-4	E-5	E-6	E-7	E-8	E-9
Linear	F	Kf	20.18	0.38	3×10^{-4}	0.03	0.05	6×10^{-6}	7×10^{-7}	8×10^{-8}
		1/n	1.73	5.13	10.63	7.35	8.12	11.73	12.90	13.77
		R²	0.78	0.92	0.87	0.81	0.94	0.87	0.83	0.89
	L	b	-0.14	-0.20	-0.23	-0.25	-0.28	-0.19	-0.18	-0.18
		qmax	-277.78	-92.59	-42.74	-34.01	-53.48	-42.19	-41.84	-29.67
		R²	0.41	0.76	0.59	0.82	0.88	0.61	0.83	0.86
Nonlinear	F	Kf	2.65	0.26	4×10^{-3}	2.15×10^{-5}	2×10^{-3}	1.22×10^{-5}	3.98×10^{-10}	5.68×10^{-10}
		1/n	1.55	3.81	7.25	11.18	9.00	9.88	16.07	15.43
		R²	0.75	0.89	0.87	0.92	0.83	0.96	0.65	0.89
	L	b	1.08×10^{-4}	5.86×10^{-6}	4.64×10^{-5}	8.27×10^{-6}	6.49×10^{-6}	4.95×10^{-6}	4.28×10^{-6}	3.42×10^{-6}
		qmax	5.42×10^4	2.46×10^6	4.1×10^5	1.17×10^6	3.53×10^6	3.47×10^6	5.08×10^6	4.13×10^6
		R²	0.75	0.95	0.93	0.70	0.73	0.92	0.50	0.67

Variable units: Kf - [(mg/g) (L/mg)$^{1/n}$]; b - L/mg; $q_{máx}$ - mg/g.

The linear model of the Langmuir isotherm showed negative values, which do not have a coherent physical meaning (Zhiltsova *et al.*, 2020). The nonlinear model had determination coefficients above 0,90 (tests E-3, E-4, and E-7), a value not reached in the linear regression model. However, some q_{max} values were very high while b values were low. These values may indicate that the Langmuir isotherm is not the most adequate to represent the adsorption of CBZ in the GAC for the analyzed conditions.

For Freundlich isotherm, the linear model had a better fit in 4 tests. The nonlinear equation had two higher determination coefficients. In the other two, fits for the linear and nonlinear were equal. Overall, considering the results of the tests, the Freundlich isotherm represented better the adsorption of CBZ on GAC than the Langmuir isotherm.

Equation 9 shows the Freundlich isotherm for the data from E-3 test for illustrative purposes. Figure 6 shows the respective Freundlich graph. The model presents a positive concavity in relation to the axes. It shows that the greater the concentration of CBZ, the higher the fraction of CBZ adsorbed on the GAC until equilibrium is reached.

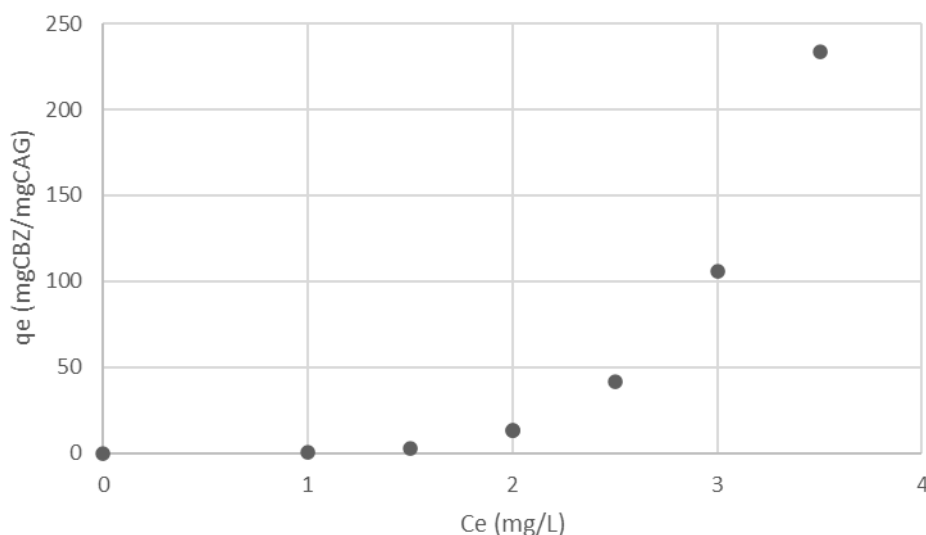$$q_e = 0.38 \cdot C_e^{5.13} \qquad \qquad \textbf{Equation (9)}$$

Figure 6. Freundlich isotherm for CBZ adsorption on granular activated carbon from Equation 9.

Freundlich's isotherm is not restricted to monolayer formation but occurs in heterogeneous multilayer formation (Haro *et al*., 2021). According to Piccin *et al*. (2017), the Freundlich isotherm assumes that the adsorption occurs heterogeneously on the surface. Thus, the adsorption of CBZ on the GAC probably occurs heterogeneously on the surface and predominantly through the formation of multilayers. This particularity does not exclude monolayer adsorption, which can also occur in the process.

Table 5 shows that almost all 1/n values were higher than unity (1/n > 1.0). This fact suggests that fungicide adsorption on the analyzed GAC is an unfavorable process (Chen *et al*., 2003; Anfar *et al*., 2020; Rizzi *et al*., 2020). Comparing the data obtained with other studies carried out with CBZ, Hgeig *et al*., (2019) found a value of 1/n equal to 0.38 for the fungicide adsorption on activated carbon produced from coffee grounds.

For other adsorbents, Jin *et al*. (2013) obtained a 1/n value of 0.71 for the adsorption of CBZ in soils composed mainly of silt, sand, clay, and a small fraction of organic matter, indicating that the adsorption in this medium is also favorable. The same was identified by Li *et al*. (2011), with 1/n <1 for all tests carried out with Burozem and Phaeozem soils at temperatures of 25° and 40°C. For polyethylene (PE) agricultural soil films (Wang *et al*., 2020) and for Sandy, Loess, and Loamy soils (Paszko, 2006), the CBZ adsorption also showed values of 1/n <1. The same was identified for the adsorption of CBZ on bentonite clay (Rizzi *et al*., 2020). However, Kanjilal *et al*. (2018) measured 1/n equal to 1.57 for the biosorption of CBZ in the strain isolated from the bacterium *Brevibacillus sp*. C17. Thus, the authors characterized CBZ biosorption as an unfavorable process considering the 1/n value.

The studies that were cited showed that the coefficient 1/n of the Freundlich model is mostly smaller than unity, indicating that CBZ adsorption is a favorable process in activated carbon from coffee grounds and soils. It is observed that the adsorption of CBZ in coconut GAC did not follow the trend observed in these studies, except for the one reported on the biosorption of the fungicide in the bacterium C17. To complement information on whether CBZ adsorption is favored in GAC for the applied conditions, Gibbs Free Energy thermodynamic analysis is discussed in sequence.

The analysis of thermodynamic parameters considered the 3.37 mg/L CBZ concentration present in water after 4 h of contact time at 30° C and 10 mg of GAC. Applying this value to Equation 10, the concentration of CBZ adsorbed on the GAC (qe) was 193.43 mgCBZ/gGAC. Substituting the values of qe and Ce in Equations 5, 6, and 7, the enthalpy, entropy, and Gibbs Free energy could be calculated. The data are presented in Table 6, considering the temperature variations of 25, 30, and 40 °C and 4h contact time for ΔG.

Table 6. Thermodynamic parameters of Carbendazim adsorption on GAC.

ΔG (kJ/mol)			ΔH (kJ/mol)	ΔS (J/mol.K)
25° C	30° C	40 ° C		
-9.62	-10.20	-8.03	-37.31	-91.84

Table 6 shows that the enthalpy variation in the CBZ adsorption process is negative, indicating that the adsorption of CBZ in coconut shell GAC is an exothermic process. The negative value of ΔG indicates the reaction is favorable. Similar results were found for adsorption of other pesticides on activated carbon, such as Atrazine, Methoxychlor, Parathion-methyl (Gupta *et al*., 2011), and Fenitrothion (Lule and Atalay, 2014).

The study by Wang *et al*. (2019) showed that the adsorption of CBZ on straw activated carbon was also characterized as an exothermic and favorable process. The same was identified in the adsorption of CBZ on activated carbon produced from coffee grounds (Hgeig *et al*. 2019), Burozem, and Phaeozem type soils (Li *et al*., 2011), and with nano-carbon (Prete *et al*., 2017). Concerning enthalpy and Gibbs free energy, the adsorption of CBZ on GAC is in accordance with reported research

The negative values of ΔG indicate that the adsorption of CBZ in GAC is a spontaneous process for all temperatures used. The lowest ΔG occurred in the test performed at the temperature of 30 °C, and the free energy decreased at 25 ℃ and 40 ℃.

It was observed that the favorable characteristic of the CBZ adsorptive process contrasts with the 1/n values of the Freundlich equation, which was higher than unity. In this research, it has been suggested that adsorption of the compound onto the adsorbent is a favorable process (Chen *et al*., 2004; Anfar *et al*., 2020; Rizzi *et al*., 2020). Therefore, the analysis of CBZ adsorption process in GAC must include not only the 1/n Freundlich coefficient but also the variation of the Gibbs free energy.

According to Zanella *et al*. (2016) and Yu *et al*. (2004), Gibbs Free Energy values between 0 to –20 kJ/mol and -80 to -400 kJ/mol generally characterize, respectively, physisorption and chemisorption processes. The values of Gibbs Free Energy measured in this study were in the range -8.03 and -10.20, suggesting that CBZ adsorption on GAC was predominantly governed by physisorption.

Physisorption or physical adsorption is when the adsorbate binds to the surface of the adsorbent due to less strong chemical bonds, such as the van der Waals forces. It is a process that occurs more quickly than chemisorption, and there is usually the formation of multilayers. Physisorption

is a reversible process that occurs at low temperatures (Rathi and Kumar, 2021). According to Ruthven (1984), some characteristics of physisorption are low heat of reaction; monolayer or multilayer adsorption; no dissociation of species involved; significant process only at low temperatures; and without electron transfer. Added to these characteristics is the predominance of permanent or induced dipole-dipole interactions between the adsorbate molecules and the adsorbent (Delle Site, 2001). The exothermic characteristic of CBZ adsorption on GAC, the predominance of physisorption, and the reasonable adjustment to the Freundlich isotherm suggest that the mentioned aspects characterize the fungicide adsorption on the studied activated carbon.

Positive values of ΔS indicate that the reaction increases the degree of disorder in the solid/solute interface during adsorption (Nekouei *et al*., 2015; Haro *et al*., 2021), with a strong affinity between the adsorbate and the adsorbent (Zanella *et al*., 2016). The value obtained for ΔS, -91.84 kJ/mol, indicates a reduction in the degree of disorder between the surface of the activated carbon and the CBZ molecules after adsorption.

Conclusions

The results showed that variations in temperature, contact time, and adsorbent mass influenced the adsorption of CBZ into GAC. The tests with 10 mg of GAC dosage presented greater efficiencies for fungicide removal. GAC dosages used in the experiments showed statistically significant results in most cases.

The application of RSM methodology found that, for the longest contact time, the adsorption of Carbendazim in coconut shell GAC was more efficient at temperatures of 25 and 30°C, characterizing an exothermic process that was later confirmed by thermodynamic analysis. The RSM curves indicated that adsorption at 25 °C and 30 °C and a contact time of 4h would achieve higher fungicide removal than at higher temperatures.

The Freundlich isotherm adjusted better to the adsorption of CBZ on GAC. In the larger part of the tests, satisfactory results were obtained by both linear and nonlinear regression models. It was found that the adsorption of the fungicide occurs predominantly in a heterogeneous and multilayered way. The Freundlich 1/n parameter presented information that contrasted with the thermodynamic analysis regarding the promotion of CBZ adsorption on GAC. The results diverge from previous studies that investigated the adsorption of CBZ on activated carbon and other adsorbents. Thus, the analysis of spontaneity should consider not only the 1/n Freundlich parameter but also the variation of the Free Energy of Gibbs, based on the conditions applied in this study. For ΔG, this study agreed with previous investigations regarding the spontaneity of the adsorptive process.

At temperatures ranging from 25º C to 40º C, the adsorption of CBZ in GAC was spontaneous. Physisorption seems to be the dominant process, with dipole-dipole interactions between the GAC surface and the fungicide. The ΔS value indicated a reduction in the degree of disorder at the adsorbent/solution interface. The fungicide adsorption on activated carbon is a reversible process without electron transfer.

The results presented in this article contribute to a better understanding of CBZ adsorption on GAC, providing support for ongoing works that aim to achieve higher CBZ removal by activated carbon in water.

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