

Utilization of acerola residue-derived biochars for methylene blue adsorption: Effects of pyrolysis temperature

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Abstract

Adsorption is an effective method for removing various types of pollutants from aqueous effluents, and the production of adsorbent materials from biomass represents a sustainable alternative. In this study, biochars produced from the pyrolysis of acerola processing residues at different temperatures were evaluated as adsorbents for methylene blue dye. Batch tests were conducted, and the results showed that the Langmuir isotherm and the pseudo-first-order kinetic model provided the best fit for the data, indicating that the adsorption process is directly proportional to the availability of active sites. The maximum removal capacity was achieved with the material produced at 400 °C (67.29 mg g⁻¹), due to its significant surface area and the presence of oxygenated functional groups, which act as active sites through hydrogen bonding and electrostatic attraction. The tested biochars demonstrated significant potential for use in adsorption processes, contributing to environmental pollution mitigation and offering a better alternative for the disposal of agro-industrial waste.

Keywords: Acerola residue; biochar; adsorption; methylene blue.

1. Introduction

The pollution of water bodies due to the discharge of untreated effluents is a problem of global relevance [1]. Among the various types of polluting compounds, organic dyes are commonly employed in several industrial processes, particularly in the textile industry, and their use generates a significant amount of contaminated wastewater [2]. These substances are potentially toxic to aquatic life, and their improper disposal can also reduce sunlight penetration in water, hindering photosynthesis and negatively impacting the ecosystem [3].

In this context, different technologies have been studied for the removal of organic dyes from wastewater before its final disposal. Due to its simplicity and effectiveness, the adsorption process is a promising alternative for removing these contaminants from aqueous effluents [4]. Alternative materials, such as biochar, a product resulting from the pyrolysis of lignocellulosic biomass, have been extensively studied for dye removal applications, mainly due to their renewable nature and low cost [5].

The industrial processes of acerola juice (*Malpighia emarginata*), a fruit with increasing and significant commercial importance in Brazil, generate a large amount of waste that can cause serious ecological problems [6]. The prospect of utilizing this biomass in biochar production is attractive from both economic and environmental perspectives, as it allows for the added value to the generated waste while reducing environmental damage [7].

Biochars possess surface characteristics that provide significant potential for use in adsorption processes. The pyrolysis temperature significantly affects these characteristics [8]. In a previous study [7], it was observed that increasing the temperature led to biochars with greater porosity and increased surface area, but in a reduction in surface functional groups, such as hydroxyl and carboxyl groups, due to their thermal degradation.

Therefore, the objective of this study is to use biochars produced from acerola residue at 300, 400, 500, 600, and 700 °C for the adsorption of methylene blue dye, evaluating the influence of temperature on the removal process.

2. Materials and Methods

2.1. Preparation of the adsorbent

The processed acerola residues were provided by the company Duas Rodas, located in the Brazilian state of Sergipe. The biomass was dried at a temperature of 50 °C for 24 h in an oven to reduce moisture content (< 10%), and subsequently ground into particles between 0.5 and 1 mm using a Willye-type mill [9].

The biochars were produced following the methodology outlined in a subsequent study, where it was applied thermochemical conversion [7]. In summary, the residue was pyrolyzed at temperatures of 300, 400, 500, and 600 °C in a rotary kiln reactor operating in continuous mode, while maintaining the following variables constant: biomass feed rate of 1.5 kg h⁻¹ with a total processing time of 20 min, drum bed rotation at 7.5 rpm, drum inclination angle of 10°, and inert gas (N₂) flow rate of 5 L min⁻¹. For the present study, it was added an additional experiment conducted at 700 °C to support the assumptions regarding the adsorption process.

Finally, the biochars were thoroughly washed using distilled water and then dried at 60 °C in an oven. Table 1 displays data on the surface area, pore volume, and oxygen content of the biochars produced at different temperatures.

Table 1. Characterization of acerola biochars

Property	Pyrolysis temperature (°C)				
	300	400	500	600	700
Surface area (m ² g ⁻¹)	9.81	60.51	112.80	272.00	301.14
Pore volume(cm ³ g ⁻¹)	0.022	0.059	0.094	0.222	0.255
O (%)	40.56	32.41	12.25	10.91	9.84

Further details regarding the pyrolytic process and detailed characterization data of the biochars can be found in the aforementioned article [7].

2.2. Adsorption assays

Batch adsorption experiments were conducted to evaluate the adsorption of methylene blue (MB). 100 mg of adsorbents were placed in contact with 10 mL of MB solution at 10, 30, 50, 100 and 150 mg L⁻¹, at times of 0, 5, 10, 15, 30 and 60 min. The experiments were conducted at room temperature (~24 °C) and at the natural pH of the solution (~6).

Absorbance readings were performed on an LGI Scientific UV-VIS spectrophotometer, at a

wavelength of 660 nm. The adsorption capacity (q , mg g⁻¹) and the removal percentage were calculated according to Equations 1 and 2, respectively.

$$q = \frac{(C_0 - C_f)V}{m} \quad (1)$$

$$\% \text{ removal} = \frac{(C_0 - C_f)}{C_0} 100 \quad (2)$$

where, C_0 is the initial concentration of the adsorbate solution (mg L⁻¹ or g L⁻¹), C_f is the final concentration of the adsorbate solution (mg L⁻¹ or g L⁻¹), V is the volume of the adsorbate solution (L) and m is the mass of the adsorbent used (g).

To evaluate the adsorption isotherms, it was used the Langmuir model (Equation 3), which assumes that adsorption occurs in a monolayer, i.e. each site can accommodate only one adsorptive entity [10], and the Freundlich model (Equation 4), an empirical equation based on multilayer adsorption, with non-uniform heat distribution [11,12].

$$q_e = \frac{q_{\max} k_L C_e}{1 + k_L C_e} \quad (3)$$

$$q_e = k_F C_e^{1/n} \quad (4)$$

where q_{\max} is the maximum amount of monolayer coverage (mg g⁻¹), k_L is the Langmuir isotherm constant (L mg⁻¹), C_e is the adsorbate concentration at equilibrium (mg L⁻¹), k_F is the Freundlich isotherm constant (mg L⁻¹)(L g⁻¹)^{1/n}, $1/n$ is the heterogeneity factor and q_e is the amount adsorbed at equilibrium (mg g⁻¹).

According to Hall *et al.* [13], the essential characteristic of the Langmuir isotherm can be expressed by the dimensionless constant R_L , called the separation factor and calculated by Equation 5, allowing the shape of the adsorption isotherm to be predicted, indicating whether the adsorption is favorable or unfavorable.

$$R_L = \frac{1}{1 + k_L C_0} \quad (5)$$

To investigate the adsorption kinetics, the pseudo-first order and pseudo-second order models were applied in their linearized forms, as described in Equations 6 and 7, respectively.

$$q_t = q_e - q_e e^{-k_1 t} \quad (6)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (7)$$

where q_t is the adsorption capacity at time t (mg g⁻¹), k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the rate

constants associated with pseudo-first order and pseudo-second order kinetics, respectively.

3. Results and Discussion

Table 2 presents the parameters obtained from fitting the experimental data using isotherm models. The analyzed parameters show that the Langmuir model ($0.91 < R^2 < 0.98$) is more suitable than the Freundlich model ($0.81 < R^2 < 0.94$) for describing the dye removal process. This suggests that the adsorption occurs in a monolayer with a uniform energy distribution on the surface. Thus, each active site can adsorb only one dye molecule, and saturation occurs when all sites are occupied, indicating that the adsorption process is homogeneous and the maximum adsorption capacity is reached when all sites are filled [10].

Table 2. Biochar isothermal parameters adsorption

T (°C)	Langmuir			Freundlich			
	q_{max} mg g ⁻¹	k_L L mg ⁻¹	R^2	R_L	n_F	k_F L g ⁻¹	R^2
300	26.62	0.70	0.96	0.90	1.50	10.11	0.94
400	67.29	0.07	0.91	0.88	1.14	4.55	0.91
500	17.19	0.17	0.97	0.89	2.44	4.01	0.89
600	11.12	0.15	0.94	0.91	3.17	3.12	0.89
700	17.12	0.07	0.98	0.84	1.99	2.21	0.81

According to Fig. 2, the value of q_{max} increases from 26.62 to 67.29 mg g⁻¹ as the pyrolysis temperature rises from 300 to 400 °C. However, as the temperature continues to increase, q_{max} shows a significant decline, reaching 17.12 mg g⁻¹ at 700 °C.

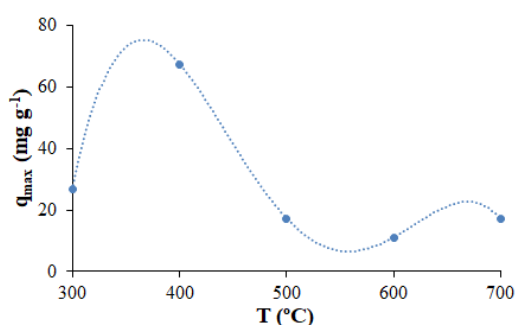


Fig. 2 q_{max} in function of the pyrolysis temperature

During the pyrolysis, the biochars surface area increases with temperature due to the formation of additional pores (Table 1). Simultaneously, the oxygen-rich functional groups, such as hydroxyls, carboxyls, and carbonyls, which play a crucial role in dye adsorption due to their ability to form hydrogen bonds and electrostatic interactions, are degraded at higher temperatures [7].

Within the temperature range of 300 to 400 °C, pore formation increases the surface area while still preserving a significant amount of oxygenated groups, which are essential for MB adsorption. However, beyond 400 °C, although the surface area continues to grow, the degradation of surface functional groups begins to outweigh the benefits of the increased surface area.

The separation factor (R_L) of the Langmuir model (Table 2) in the range of $0 < R_L < 1$, indicates that the dye adsorption is a favorable process.

Regarding kinetics (Table 3), it was observed that equilibrium is reached quickly for all the produced biochars, and that the amount of dye adsorbed increases when using solutions with higher initial concentrations.

Table 3. Biochar kinetic model parameters

300 °C MB mg L ⁻¹	Pseudo first order			Pseudo second order		
	k_1 min ⁻¹	q_e mg g ⁻¹	R^2	k_2 g mg ⁻¹ min ⁻¹	q_e mg g ⁻¹	R^2
10	0.39	1.80	0.94	0.27	1.97	0.87
30	0.45	0.93	0.92	0.60	1.01	0.83
50	0.37	4.69	0.95	0.10	5.17	0.90
100	0.39	13.46	0.95	0.04	14.76	0.88
150	0.33	7.77	0.96	0.05	8.57	0.92
400 °C MB mg L ⁻¹	Pseudo first order			Pseudo second order		
	k_1 min ⁻¹	q_e mg g ⁻¹	R^2	k_2 g mg ⁻¹ min ⁻¹	q_e mg g ⁻¹	R^2
10	0.13	2.25	0.90	0.05	2.66	0.87
30	0.39	8.21	0.94	0.05	9.06	0.89
50	0.35	14.17	0.96	0.03	15.64	0.91
100	0.21	51.23	0.98	0.01	57.36	0.96
150	0.10	92.20	0.99	0.00	109.8	0.98
500 °C MB mg L ⁻¹	Pseudo first order			Pseudo second order		
	k_1 min ⁻¹	q_e mg g ⁻¹	R^2	k_2 g mg ⁻¹ min ⁻¹	q_e mg g ⁻¹	R^2
10	-	-	-	-	-	-
30	0.42	3.17	0.93	0.16	3.48	0.86
50	0.35	6.20	0.96	0.07	6.84	0.91
100	0.35	30.19	0.95	0.01	33.64	0.91
150	0.16	44.52	0.96	0.004	51.23	0.96
600 °C MB mg L ⁻¹	Pseudo first order			Pseudo second order		
	k_1 min ⁻¹	q_e mg g ⁻¹	R^2	k_2 g mg ⁻¹ min ⁻¹	q_e mg g ⁻¹	R^2
10	-	-	-	-	-	-
30	0.14	1.06	0.99	0.14	1.22	0.97
50	0.33	9.88	0.96	0.04	10.97	0.92
100	0.20	20.53	0.96	0.01	23.30	0.96
150	0.07	30.93	0.95	0.002	38.30	0.93
700 °C MB mg L ⁻¹	Pseudo first order			Pseudo second order		
	k_1 min ⁻¹	q_e mg g ⁻¹	R^2	k_2 g mg ⁻¹ min ⁻¹	q_e mg g ⁻¹	R^2
10	-	-	-	-	-	-
30	0.06	0.38	0.90	0.11	0.50	0.91
50	0.04	4.54	0.95	0.004	7.24	0.95
100	0.30	22.10	0.97	0.017	24.38	0.92
150	0.14	35.49	0.95	0.005	40.03	0.91

Within the first 30 s, a considerable amount of dye was already adsorbed, demonstrating the

rapidity of the process. This high adsorption rate in the initial moments of the tests likely resulted from a combination of mechanisms involving electrostatic attraction between the dye molecules and the surface functional groups present in the biochars, as well as adhesion involving the pore structures within the material [14].

The results show that both kinetic models describe the data well. However, the model that provides the best fit is the pseudo-first-order model. This indicates that the adsorption process is controlled by the diffusion of the dye to the active sites on the biochar surface. According to this model, the adsorption capacity and the amount of active sites are directly proportional [15]. At the beginning of the batch process, there is a rapid adsorption of the dye due to the high number of available active sites, and as these sites become occupied, the rate of adsorption decreases.

4. Conclusion

Biochars produced from the pyrolysis of acerola industrial residue at various temperatures were evaluated as adsorbents for MB dye. The Langmuir model best fit the data, indicating monolayer adsorption on a uniform surface. The maximum adsorption capacity increased significantly from 300 to 400 °C, reaching 67.29 mg g⁻¹, but decreased at higher temperatures due to the degradation of oxygenated functional groups. The biochar produced at 400 °C demonstrated the best balance between surface area and functional group preservation. These findings underscore the potential of this biochar as an effective and sustainable material for effluent treatment.

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References

- [1] Tejada-Tovar C, Villabona-Ortíz Á, Ortega-Toro R. Removal of metals and dyes in water using low-cost agro-industrial waste materials. *Appl Sci* 2023, 13(14): 8481.
- [2] Ravindran G, Jeyaraju RM, Nandipati G, Seerangounder S, Al-Zaqri N, Boshala A, Hayder G. Prevention of groundwater contamination from the pollutants released from dyeing industries using biochar produced from palm shell. *Urban Clim* 2023, 49: 101515.
- [3] Li L, Liu F, Duan H, Wang X, Li J, Wang Y, Luo C. The preparation of novel adsorbent materials with efficient adsorption performance for both chromium and methylene blue. *Colloid Surface B* 2016, 141:253-259.
- [4] Martínez RJ, Vela-Carrillo AZ, Godínez LA, Perez-Bom JJ, Robles I. Competitive adsorption of anionic and cationic molecules on three activated carbons derived from agroindustrial waste. *Biomass Bioenerg* 2023, 168:106660.
- [5] Ahmed MJ, Okoye PU, Hummadi EH, Hameed BH. High-performance porous biochar from the pyrolysis of natural and renewable seaweed (*Gelidiella acerosa*) and its application for the adsorption of methylene blue. *Bioresource Technol* 2019, 278: 159-164.
- [6] Costa GCC, Altino HON, Duarte CR, Hori CE, Barrozo MAS. Hydrothermal carbonization of acerola (*Malpighia Emarginata*. D.C.) waste pretreated with supercritical CO₂ and zinc chloride as an additive. *J Supercrit Fluid* 2024, 209: 106234.
- [7] Silva JDO, Wisniewski JÁ, Carregosa ISC, Silva WR, Abud AKS, Oliveira Júnior AM. Thermovalorization of acerola industrial waste by pyrolysis in a continuous rotary kiln reactor. *J Anal Appl Pyrol* 2022, 161: 105373.
- [8] Mahdi Z, Hanandeh AE, Yu Q. Influence of pyrolysis conditions on surface characteristics and methylene blue adsorption of biochar derived from date seed biomass. *Waste Biomass Valori* 2017, 8(6): 2061-2073.
- [9] Silva JDO, Santos DEL, Abud AKS, Oliveira Júnior AM. Characterization of acerola (*Malpighia emarginata*) industrial waste as raw material for thermochemical processes. *Waste Manage* 2020, 107: 143-149.
- [10] Langmuir I. The adsorption of gases on plane surfaces of glass, mica, and platinum. *J Am Chem Soc* 1918, 40: 1361-1403.
- [11] Freundlich H. Over the adsorption in solution. *J Phys Chem* 1906, 57:1100-1107.
- [12] El Haddad M, Regti A, Laamari MR, Slimani R, Mamouni R, El Antri S, Lazar S. Calcined mussel shells as a new and eco-friendly biosorbent to remove textile dyes from aqueous solutions. *J Taiwan Inst Chem E* 2014; 45: 533-540.
- [13] Hall KR, Eagleton LC, Acrivos A, Vermeulen T. Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. *Ind Eng Chem Fund* 1966, 5: 212-219.
- [14] Deng H, Lu J, Li G, Zhang G, Wang X. Adsorption of methylene blue on adsorbent materials produced from cotton stalk. *Chem Eng J* 2011, 172(1): 326-334.
- [15] Bhagavathi PT, Nagalingam R, Saravanan P. Batch and column studies on removal of methylene blue dye by microalgae biochar. *Biomass Conv Bioref* 2022, 13: 10327-10342.