Production of biochar derived from swine sludge modified with CaO for removal of methylene blue from water

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Abstract: Water pollution by dyes such as methylene blue is still a concern around the world, given the effects that exposure to these contaminants can have on health. In this work, a biochar derived from swine sludge was developed, and subsequently modified with calcium oxide, as a material with potential for removing methylene blue dye from aqueous solutions. There are still no reports in the literature on the production of biochar from swine sludge, followed by modification with calcium oxide, used as a methylene blue adsorbent. The effect of pH, adsorbent dosage, adsorption kinetics and adsorption isotherm were investigated. Satisfactory adsorption was obtained at pH 7 at a temperature of 303 K, where an adsorption capacity of 14.43 mg g-1 was experimentally obtained under these conditions. The ideal adsorbent dosage was 0.93 g L-1. The model that best described the kinetic data was the Pseudo first order model, which presented an R^2 of 99.27. Satisfactory adsorption of methylene blue was achieved at pH 7 and 303 K, with a maximum adsorption capacity of 86.14 mg g^{-1}, according to the Liu model. The results demonstrate the feasibility of using biochar modified with calcium oxide to remove methylene blue dye from aqueous solutions. Furthermore, the production of biochar from swine sludge represents a way of valuing this waste that is often discarded inappropriately.

Keywords: Biochar; swine sludge; adsorption; methylene blue; dye removal.

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1 Introduction

The expansion of swine production has led to a significant increase in the generation of manure as a by-product, posing ongoing challenges for its proper disposal around the world. After composting, animal waste is commonly used as organic fertilizer on agricultural land, which can actually improve soil fertility and quality [1]. Nonetheless, there are associated risks, including the elevated electrical conductivity of organic material, which may elevate soil salinity, and the high concentrations of $N\text{-}NO_3$, prone to leaching into superficial and underground water sources [2]. To stabilize heavy metals and reduce their availability, thermochemical treatments like pyrolysis and hydrothermal treatment are employed [3].

Methylene blue (MB) stands as the most utilized dye in the dyeing of materials such as cotton, wood, and silk [4]. Mismanagement of effluents containing dyes not only contributes to generate environmental problems but also poses risks to human health. Continuous and prolonged consumption of water tainted with dyes can result in adverse effects on the human body, including skin irritation, neurological damage, and severe harm to the liver and digestive system [5]. To prevent such risks, it is imperative to eliminate this dye from water sources. Dye removal generally involves a complex and diverse set of physicochemical and biological processes, and, among the available treatment methods, the adsorption of contaminants using activated carbon has gained considerable interest [6].

In recent years, biochar has been widely studied due to its potential for adsorption of heavy metals and dyes. This is due to its low cost and the variety of raw materials available [7]. For example, researchers have explored the use of acid $(NH_4)_2S_2O_8$ modified sludge biochar for the adsorption of methylene blue and Cr(VI) [7], as well as thiourea-modified biochar for the removal of Pb(II) from wastewater [8], and removal of methylene blue from aqueous solution by biochar derived from sewage sludge [9]. Although there are several studies on the production of biochar with the purpose of removing dyes and heavy metals from aqueous solutions, there are still no reports in the literature on the production of biochar from swine sludge, subsequently modified with calcium oxide, for use in adsorption of methylene blue.

Hence, the primary aim of this study was to produce biochar from swine sludge via pyrolysis, subsequently modifying it with calcium oxide for application in removing methylene blue from aqueous solutions. Adsorption experiments were conducted using

methylene blue solution, wherein the effect of pH, dosage of adsorbent, adsorption kinetics and adsorption isotherm were assessed.

2 Materials and methods

2.1 Materials

The swine sludge was obtained from the Swine Laboratory of the Department of Zootechny of the Federal University of Santa Maria. Calcium oxide was obtained from Dinâmica (Indaiatuba, Brazil). Methylene blue was obtained from Dinâmica (Indaiatuba, Brazil). Nitric acid and sodium hydroxide were obtained from Synth (Diadema, Brazil).

2.2 Preparation of BC-CaO

Firstly, the swine sludge was dried in an oven at a temperature of 105 ºC for 12 hours. After drying, pyrolysis was carried out in a tubular oven and operating conditions were set at 550 ºC, 120 minutes under N_2 atmosphere and heating rate of 15 ºC min^{-1}[10].

Then, modification was carried out with calcium oxide. The moisture content of biochar was adjusted to 80% with water, and then CaO was added to the biochar at a ratio of 5% m/m CaO/biochar [11]. The mixture was kept under stirring at 130 rpm at 25ºC. And then drying was carried out in an oven at 60 ºC [11]. Therefore, biochar modified with calcium oxide (BC-CaO) was obtained.

2.4 Batch adsorption experiments

The adsorption experiments were carried out in batch, using 46.6 mg of BC-CaO and 50 mL of methylene blue solution, corresponding to an adsorbent dosage of 0.93 g L^{-1}. A temperature-controlled shaker (SL-222, Solab, Piracicaba, Brazil) was used in these experiments.

Initially, the effect of pH on adsorption was evaluated, varying the pH from 3 to 11, and adjusted with solutions of 0.1 M NaOH and 0.1 M HNO_3 [9]. The contact time was 4 h, at a temperature of 30 ºC, and initial concentration of methylene blue in solution was 50 mg L^{-1} [12].

After determining the optimum pH for adsorption of the methylene blue dye, the kinetic study was carried out, maintaining the initial concentration of methylene blue at 50 mg L^{-1} and varying the contact time from 0 to 240 minutes, at 30 ºC. Once the adsorption equilibrium time was defined, the equilibrium curve was constructed at a temperature of 30 ºC, pH 7, and the concentration of methylene blue in solution varied between 10 and 500 mg L^{-1}.

At the end of each adsorption test, the samples were filtered, and the absorbance was determined using the UV–Visible spectrophotometer (Shimadzu, UVmini-1240, Japan), at a wavelength of 665 nm [9].

The methylene blue removal percentage (R%) and the adsorption capacity (q_e) were calculated using Equations 1 and 2, respectively:

$$R\% = \frac{(C_0 - C_e)}{C_0} \cdot 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)}{m} \cdot V \quad (2)$$

where, C_0 is the initial concentration of methylene blue in the aqueous solution (mg L^{-1}), C_e is the methylene blue concentration at equilibrium (mg L^{-1}), m is the mass of adsorbent (g), and V is the solution volume (L).

2.5 Kinetic models

A kinetic study of methylene blue adsorption on the BC-CaO was performed using the pseudo-first order (PFO) and pseudo-second order (PSO) models, described by Equations 3 and 4, respectively [13]:

$$q_t = q_1(1 - e^{-k_1 t}) \quad (3)$$

$$q_t = \frac{k_2 q_2^2 t}{(1 + k_2 q_2 t)} \quad (4)$$

where, q_t is the adsorption capacity at time t (mg g^{-1}), q_1 and q_2 (mg g^{-1}) are the theoretical adsorption capacities for the PFO and PSO models, respectively, and k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the adsorption rate constants for the PFO and PSO models, respectively.

2.5 Isotherm models

The equilibrium curve for methylene blue adsorption by BC-CaO was fitted using the Langmuir, Freundlich, and Liu adsorption isotherm models, described by Equations 5, 6, and 7, respectively [14, 15, 16]:

$$q_e = \frac{q_{m_L} K_L C_e}{1 + K_L C_e} \quad (5)$$

$$q_e = K_F C_e^{1/n_F} \quad (6)$$

$$q_e = \frac{q_{max}(K_g C_e)^{nL}}{1 + (K_g C_e)^{nL}} \quad (7)$$

where, C_e is the solution concentration at equilibrium (mg L^{-1}), K_L is the Langmuir constant (L mg^{-1}), q_{mL} is the maximum adsorption capacity for the Langmuir model (mg g^{-1}), K_F is the Freundlich constant ((mg g^{-1}) (mg $L^{-1})^{-1/nF}$), $1/n_F$ is the heterogeneity factor, k_g is the Liu equilibrium constant (L mg^{-1}); n_L is dimensionless exponent of the Liu equation, and q_{max} is the maximum adsorption capacity of the adsorbent (mg g^{-1}).

3 Results and discussion

3.1 Effect of pH and adsorbent dosage

Figure 1(a) shows the effect of pH on adsorption of methylene blue by the BC-CaO. The pH ranges from 3 to 11. As the pH was increased from 3 to 11, the adsorption capacity increased from 1.09 to 15.48 mg g^{-1}, respectively. At low pH, H^+ ions occupied the limited binding sites in sludge-derived biochar, hindering the adsorption of MB, a cationic dye with a positive electrical charge on the surface. Therefore, at low pH, MB suffered a repulsive interaction with H^+ ions, which made its adsorption on biochar difficult [9]. As the pH increases, the concentration of H^+ ions in the solution decreases, reducing competition for adsorption. Consequently, the repulsive interactions between methylene blue and H^+ ions decrease, favoring the adsorption of methylene blue [9]. Therefore, the subsequent experiments were performed at pH 7.

Figure 1(b) shows the adsorbent dosage on adsorption of methylene blue by the BC-CaO. It is observed that as the adsorbent dosage increased (0.5 to 1.5 g L^{-1}), the removal percentage also increased (53.85 – 77.89 %). This occurs due to an increase in the adsorbent surface area and a greater number of active sites available for adsorption

[10]. However, there is a decrease in adsorption capacity (21.96 – 10.58 mg g^{-1}) with increasing adsorbent dosage, which can be attributed to a greater number of active sites on the adsorbent that remain unsaturated during adsorption of methylene blue [10]. Therefore, the optimal adsorbent dosage was 0.93 g L^{-1}.

3.4 Adsorption kinetics

The kinetic curves for the adsorption of methylene blue by the BC-CaO are shown in Figure 1(c). It is possible to observe that there was rapid adsorption in the first 10 minutes, followed by a decrease as equilibrium was reached after 20 minutes. Zhao et al. also reported a rapid removal of methylene blue in the first 20 minutes. The faster adsorption at the beginning can be attributed to the greater availability of BC-CaO active sites, and the greater driving force [7].

Table 1 presents the kinetic parameters for adsorption of methylene blue by BC-CaO. The model that best adjusted the kinetic data was the Pseudo-first order model, with a higher R^2 value, compared to the Pseudo-second order model. The PFO model also presented a lower average relative error (ARE) than the PSO model.

Table 1. Kinetic parameters for adsorption of methylene blue by the BC-CaO.

Pseudo-first order (PFO) model		**Pseudo-second order (PSO) model**	
q_1 (mg g^{-1})	11.90	q_2 (mg g^{-1})	11.96
k_1 (min^{-1})	0.73	k_2 (g mg^{-1} min^{-1})	0.34
R^2 (%)	99.27	R^2 (%)	98.65
R^2_{adj} (%)	99.18	R^2_{adj} (%)	98.48
ARE (%)	22.81	ARE (%)	33.21

3.4 Adsorption isotherm

Figure 1(d) shows the isotherm curve for the adsorption of methylene blue by the BC-CaO at 303 K. The curve shows type I behavior, according to the IUPAC classification [17]. In this type of isotherm curve, there is a sloped portion at low equilibrium concentrations, indicating high adsorption capacities. However, at high

equilibrium concentrations, the formation of a plateau can be observed, suggesting a reduced adsorption capacity [18].

The isotherm curve was described using the Langmuir, Freundlich, and Liu models. The equilibrium parameter values for the adsorption of methylene blue by BC-CaO are shown in Table 2. The selection of the best model was determined by considering the coefficient of determination (R^2) and reduced chi-square. Based on these criteria, the Liu model exhibited the highest R^2 value and the lowest reduced chi-square, indicating the best fit to the equilibrium data.

The Liu isotherm model is a hybrid of the Langmuir and Freundlich isotherm models, but it discards the monolayer assumption of the Langmuir model and the infinite adsorption assumption of the Freundlich model [16]. According to the Liu model, the active sites of the adsorbent cannot have the same energy [16].

Table 2. Equilibrium parameter values for adsorption of methylene blue by the BC-CaO.

Isotherm model	Temperature (K)
	303
Langmuir	
q_{mL} (mg g^{-1})	72.90
K_L (L mg^{-1})	0.06
R^2	0.97
R^2_{adj}	0.96
Reduced chi-square	9.62
Freundlich	
K_F ((mg g^{-1}) (mg L^{-1})$^{-1/nF}$)	20.11
$1/n_F$	0.23
R^2	0.94
R^2_{adj}	0.93
Reduced chi-square	18.86
Liu	
$Q_{máx}$ (mg g^{-1})	86.14
Kg (L mg^{-1})	0.04
n_L	0.65
R^2	0.99
R^2_{adj}	0.99

Reduced chi-square	2.63

According to the Liu model, the maximum methylene blue adsorption capacity by the BC-CaO was 86.14 mg g^{-1}.

Table 3 provides a comparison of the methylene blue adsorption capacities of the BC-CaO and other adsorbents used for methylene blue recovery.

Table 3. Maximum adsorption capacities of different systems used for the adsorption of methylene blue.

Adsorbent	Model	pH	T (K)	q_m (mg g^{-1})	Reference
BC-CaO	Liu	7	303	86.14	This work.
Modified bagasse fly ash	Langmuir	9.6	-	5.19	(Meskel et al., 2024[19])
Walnut shell	Langmuir	8	303	36.63	(Uddin and Nasar, 2020[20])
Potato peel (acid treated)	Langmuir	12	298	41.6	(Tiwari et al., 2015[21])
Potato peel (formaldehyde treated)	Langmuir	8	298	47.62	(Tiwari et al., 2015[21])
Bagasse (tartaric acid treated)	Langmuir	9	303	59.88	(Low et al., 2012)[22]

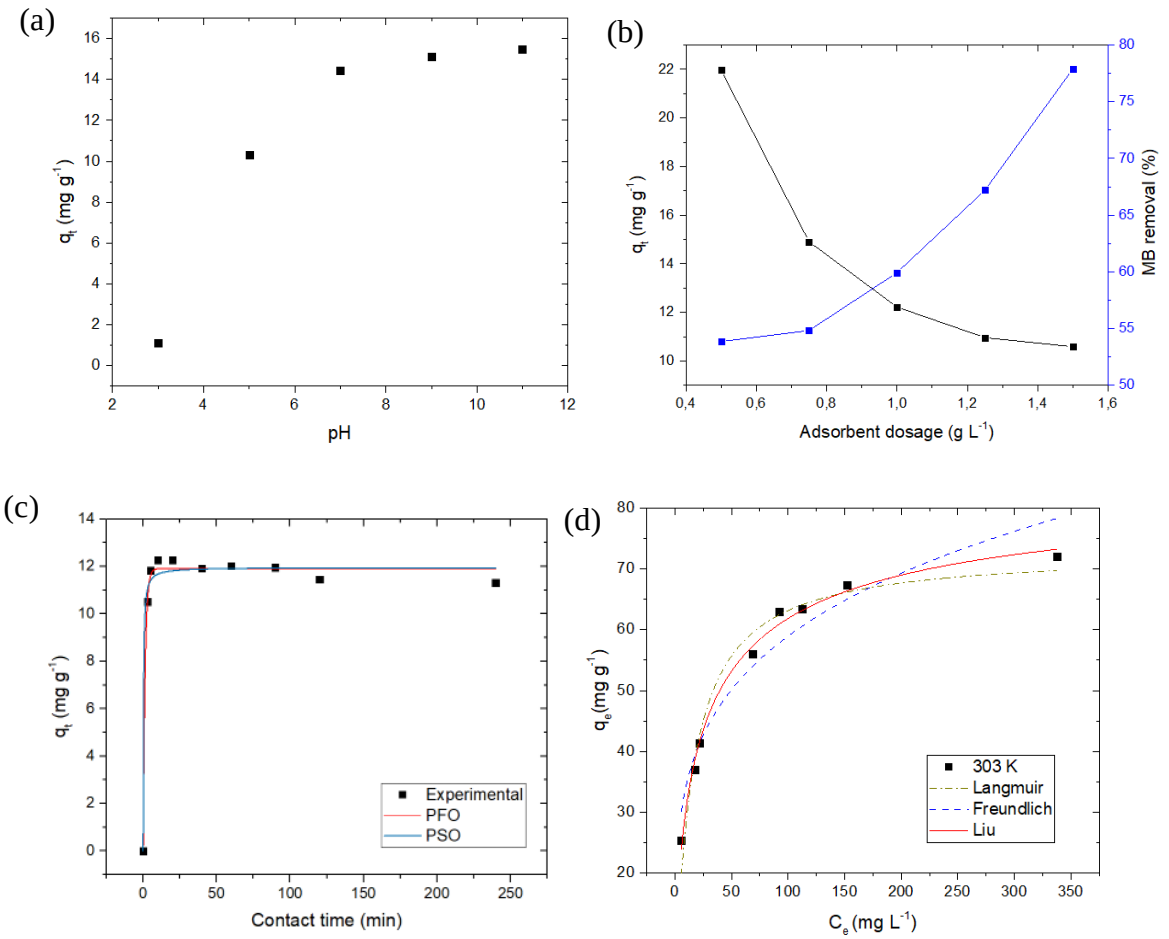

Figure 1. (a) Effect of pH on the adsorption of methylene blue by the BC-CaO. Experimental conditions: t = 240 min, T = 303 K, C_0 = 50 mg L^{-1}, m = 25 mg, and V = 50 mL; (b) effect adsorbent dosage on the adsorption of methylene blue by the BC-CaO. Experimental conditions: t = 240 min, T = 303 K, C_0 = 50 mg L^{-1} and V = 50 mL; (c) kinetic curves for the adsorption of methylene blue by BC-CaO. Experimental conditions: T = 303 K, C_0 = 50 mg L^{-1}, m = 46.6 mg, and V = 50 mL and (d) Isotherm curve for the adsorption of methylene blue by BC-CaO. Experimental conditions: T = 303 K, C_0 = 10-500 mg L^{-1}, m = 46.6 mg, and V = 50 mL.

The results of this study highlight the significant potential of biochar derived from swine sludge, modified with calcium oxide, as an efficient adsorbent of methylene blue dye. This discovery not only highlights biochar's ability to promote efficient pollutant removal, but also highlights the opportunity to add value to a waste that is often inappropriately disposed of, such as swine sludge. By converting this waste into a valuable and useful material, not only is pollution mitigated, but paths to sustainable and economically beneficial alternatives are also opened.

4 Conclusions

Activated carbon was successfully produced through the pyrolysis process, followed by modification with calcium oxide. The adsorption experiments were successfully conducted, where the effect of pH, adsorbent dosage and adsorption kinetics were evaluated. After analyzing the effect of pH, the pH 7 was selected to study the adsorbent dosage and adsorption kinetics. The optimal adsorbent dosage chosen to carry out the kinetic study was 0.93 g L^{-1}. It was observed that adsorption equilibrium was reached in approximately 20 minutes. The pseudo-first order model proved to be the one that best fitted the kinetic data. Satisfactory adsorption of methylene blue was achieved at pH 7 and 303 K, with a maximum adsorption capacity of 86.14 mg g^{-1}, according to the Liu model.

The results presented in this work show the feasibility of applying biochar modified with calcium oxide to remove methylene blue dye from aqueous solutions, as preliminary tests showed that the adsorption capacity of the material increased two times when modifying the biochar with calcium oxide. Furthermore, the production of biochar from swine sludge is a way of adding value to this waste, which is often incorrectly disposed of.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this manuscript.

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