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<https://pubs.acs.org/doi/10.1021/acs.iecr.8b03734>

DOI: 10.1021/acs.iecr.8b03734

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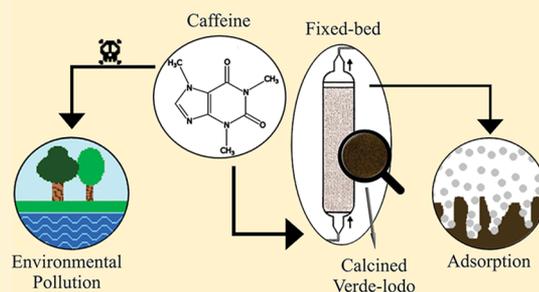
Fixed-Bed Adsorption of Caffeine onto Thermally Modified Verde-lodo Bentonite

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Supporting Information

ABSTRACT: Only a few studies regarding the adsorption of caffeine have been published in the past years, and none of them has evaluated the fixed-bed adsorption of a pharmaceutical using bentonite. This work evaluated caffeine adsorption using the thermally modified bentonite Verde-lodo as adsorbent. The effects of flow operating rate and inlet caffeine concentration have been investigated through breakthrough curves. Mass transfer and efficiency parameters were calculated for each operating condition. The results obtained at $1 \text{ mL}\cdot\text{min}^{-1}$ and $0.2 \text{ mmol}\cdot\text{L}^{-1}$ showed a breakthrough time of over 150 h and a removal percentage of approximately 100% until breakthrough. The highest breakthrough and saturation adsorption capacities were 0.122 and $0.219 \text{ mmol}\cdot\text{g}^{-1}$, respectively, for the operating condition of $1 \text{ mL}\cdot\text{min}^{-1}$ and $1.0 \text{ mmol}\cdot\text{L}^{-1}$. The breakthrough curves were remarkably described ($R^2 > 0.975$) by Thomas, Yoon, and Nelson, and modified dose–response models. Moreover, thermal, X-ray diffraction, Fourier transformed infrared spectroscopy, and scanning electron microscopy analyses were performed in order to compare the calcined Verde-lodo clay before and after caffeine adsorption, and they indicated the presence of the compound in the adsorbent.



1. INTRODUCTION

With the development of new analytical technologies, a new group of contaminants, present in water at low concentrations, usually between nanograms and micrograms per liter ($\text{ng}\cdot\text{L}^{-1}$ – $\mu\text{g}\cdot\text{L}^{-1}$), began to be detected. Owing to their toxicity, these contaminants, a group of microorganisms and natural or synthetic chemicals, became known as emerging contaminants.^{1,2}

One of the most commonly detected emerging contaminant is caffeine, the world's most consumed psychoactive stimulant. Widely used by the pharmaceutical industry in manufacturing different drugs,^{3,4} the substance is also found in beverages and food, such as tea, coffee and chocolate. After its ingestion, caffeine is absorbed and distributed in the organism,⁵ and the unmetabolized substance is excreted via urine and feces of humans and animals,⁶ reaching the water bodies as any other emerging contaminant.

Although caffeine is not toxic to humans at the concentrations detected in water bodies, there are reports pointing to the substance as being capable of causing harmful effects to the reproductive system of small aquatic animals, even at low concentrations.^{7–9} A study published by Frédéric and Yves¹⁰ pointed to caffeine as the 20th most hazardous pharmaceuticals in a group of 127 investigated.

Many emerging contaminants, including caffeine, are recalcitrant to the usual processes employed in drinking water and wastewater treatment plants, and continue present in water even after the treatment. Another source of contami-

nation is the discharge of raw sewage in water bodies.^{1,11} There are different alternative technologies that have already been studied for emerging contaminants removal, but adsorption is noteworthy due to its lower cost of implementation and operation, simplicity of operation and efficiency in the removal of highly diluted compounds.^{1,12}

When adsorption occurs as part of a commercial process, it usually occurs in bed columns and, although there are applications for moving-beds, the fixed-bed is the most widely used type of system.¹³ Most of the studies on caffeine adsorption, however, are restricted to a batch removal study and do not evaluate the removal of the compound in the fixed-bed.¹⁴ The study of adsorption in a fixed-bed at the laboratory-scale is important because the obtained parameters are easily scaled up to be used in large-scale wastewater treatment.¹⁵

The use of activated carbons for caffeine adsorption has already been studied.^{14,16,17} However, the proposal of this paper is to investigate the adsorption of caffeine using an alternative adsorbent, abundant and cheaper than activated carbon, since its high cost can make the adsorption process economically unfeasible. Among different classes of alternative adsorbent, clay materials occur in most continents and present high specific area, great mechanical and chemical stability.^{1,18}

Received: August 6, 2018

Revised: November 23, 2018

Accepted: November 30, 2018

Published: November 30, 2018

Table 1. Characterization Analysis Performed on Bentonite CVL before and after Caffeine Adsorption

analyze	equipment	parameters/observation
thermal analysis (TG/DTG and DTA)	Shimadzu, model DTG-60	material heated from room temperature to 1000 °C at 10 °C per minute, with a flow of N ₂ at 50 mL·min ⁻¹
X-ray diffraction (XRD)	Philips, model X'Pert-MPD	particle diameter lower than 0.074 mm, Cu K α adsorption, 40 kV, 40 mA, step size of 0.02°, velocity of 0.02°·s ⁻¹ , angle of incidence from 3 to 90°
Fourier transformed infrared spectroscopy (FTIR)	Thermo Scientific, model Nicolet 6700	samples analyzed as KBr pastilles, at wavelengths in the range of 4000 to 400 cm ⁻¹
scanning electron microscopy (SEM)	LEO, model 440i	particles covered with a thin layer of gold, zoom of 1000X

There are several studies using the bentonite Verde-lodo as an adsorbent in the removal of different contaminants in diluted aqueous systems. The material has characteristics favorable to adsorption, such as high specific surface area and porosity, besides being abundant in nature and cheaper than activated carbon.¹⁹ In previous works, Verde-lodo clay was modified with cetylpyridinium chloride and benzalkonium chloride and used to remove benzene, toluene, and xylene,¹⁹ and its thermally modified form was used to remove metallic ions.^{20–22} Because of the affinity between the thermally modified Verde-lodo and some pharmaceutical compounds, including caffeine,²³ the material was selected for the current study.

This work aims investigate the caffeine adsorption in aqueous solution in a fixed-bed system. The study includes a part involving tests with variations of inlet flow and concentration, and a part involving the mathematical modeling of the obtained data. To the best of the authors' knowledge, there are still no studies published in the literature, in the field of emerging contaminants, about caffeine adsorption in fixed-beds using bentonites.

2. MATERIAL AND METHODS

Caffeine Solutions Preparation. The caffeine solutions were prepared by diluting a stock solution of high purity grade (>99.9%) caffeine (from Ranko International) in deionized water. The absorbance values were obtained with a UV–vis spectrophotometer (UVmini-1240, Shimadzu) at $\lambda_{\max} = 273$ nm.

Adsorbent Preparation. Verde-lodo bentonite clay, from the state of Paraíba (Brazil), was provided in its raw form (powder) by Dolomil Industrial Ltda. The material was wetted, dried, crushed, and sieved at particles with an average size of 0.855 mm. The calcination was performed in a muffle furnace (Quimis) for 24 h at 500 °C, which are the best conditions for calcination of Verde-lodo clay, since they are responsible for the increase of its mechanic resistance.²⁰ Previous BET analysis of Verde-lodo indicated a specific surface area of 64.31 m²·g⁻¹ before calcination and 62.08 m²·g⁻¹ after calcination.²⁰ Even with a slightly smaller surface area, the use of the CVL instead of its raw form is recommended for adsorption because, besides the increase in the material's resistance, without calcination the bentonite expands when it is in contact with water and, consequently, cannot be used in fixed-bed systems.

Clay Characterization. Characterization analyses were performed in order to verify the properties of CVL before and after caffeine adsorption. Table 1 summarizes the employed techniques.

Fixed-Bed Adsorption. The prepared clay was packed in a cylindrical glass column, 14 cm high and 1.4 cm in diameter. The top of the bed was covered with glass wool and a stopper to close the column and avoid the loss of adsorbent during the

experiments. To avoid the exit of clay particles in the bed effluent, which could interfere in the analysis of results, the packed bed was washed with deionized water in an upward continuous flow until the bed effluent showed no more clay particles. After this step, the solution with the adsorbate was also injected in ascending and continuous flow. The fluids were injected in the column using a peristaltic pump (7523-80, Masterflex, USA) connected to precision pump tubing (1.4 mm of internal diameter).

One of the many advantages of the adsorption process is the possibility of removing a contaminant without exposing the system to harmful chemicals or complex environmental conditions.²⁴ For this reason, the prepared set was kept in a room with controlled temperature (approximately 25 °C), so the temperature evaluated was as close as possible to the ones of the actual wastewaters containing caffeine in Brazil, what can lead to energy savings in large scale systems. For the same reasons, the pH was not controlled and was kept natural (between 5.5 and 7.5), without the need of adding acids or bases to the system. In addition, a previous study concluded that the adsorption of caffeine using CVL is not affected by pH values from 3.6 up to 10.4.²⁵

Effluent samples were collected at predetermined times using a Gilson automatic fraction collector (FC 203B). When the samples were not being collected, the effluent was stored in a container for proper discharge. The whole procedure was performed at three different flow rates (5 mL·min⁻¹, 3 mL·min⁻¹ and 1 mL·min⁻¹) at a concentration of 1.0 mmol·L⁻¹ (194.19 mg·L⁻¹). The best flow rate (1 mL·min⁻¹) was used to test the effect of inlet concentration (0.6 mmol·L⁻¹ (116.51 mg·L⁻¹) and 0.2 mmol·L⁻¹ (38.84 mg·L⁻¹)), and to determine the mass transfer and efficiency parameters of each operating condition. Each run (combination of flow rate and concentration) was performed once.

The efficiency parameters of the obtained breakthrough curves were calculated using eqs 1–5.²⁶

$$q_u = \frac{C_0 Q}{m} \int_0^{t_b} 1 - \frac{C(t)}{C_0} dt \quad (1)$$

$$q_t = \frac{C_0 Q}{m} \int_0^{\infty} 1 - \frac{C(t)}{C_0} dt \quad (2)$$

$$h_{MTZ} = \left(1 - \frac{q_u}{q_t} \right) H_b \quad (3)$$

$$REM_b(\%) = \left(\frac{q_u m}{C_0 Q t_b} \right) \quad (4)$$

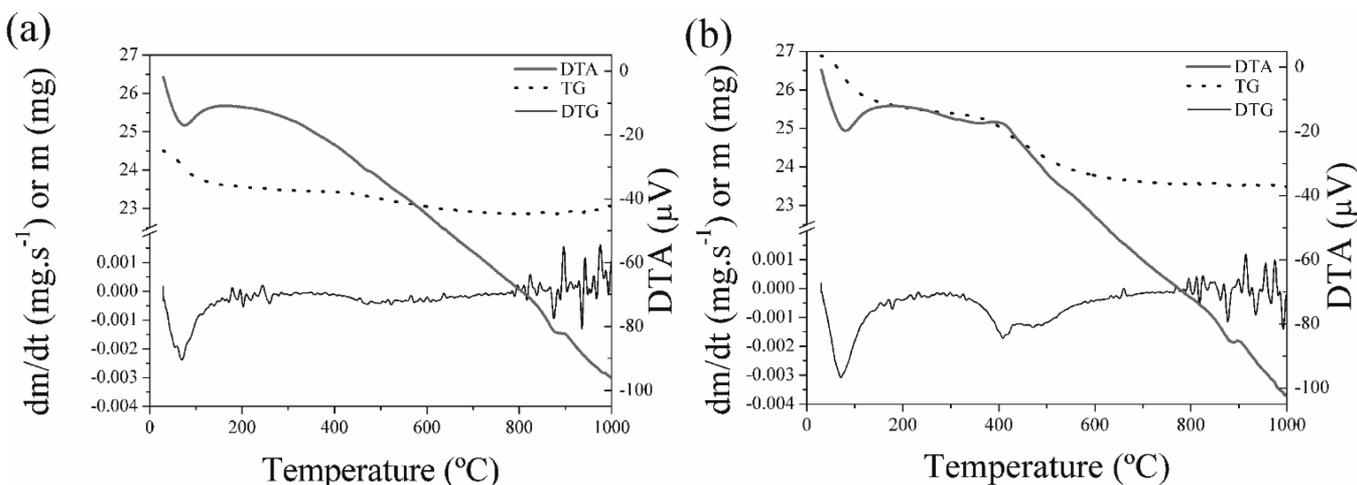


Figure 1. Thermal analysis (TG/DTG and TGA) curves for CVL before (a) and after (b) caffeine adsorption. Material heated from room temperature to 1000 °C at 10 °C per minute.

$$\text{REM}_e(\%) = \left(\frac{q_t m}{C_0 Q t_e} \right) \quad (5)$$

where q_u is the breakthrough adsorption capacity ($\text{mmol}\cdot\text{g}^{-1}$), q_t is the saturation adsorption capacity ($\text{mmol}\cdot\text{g}^{-1}$), C_0 is the adsorbate initial concentration ($\text{mmol}\cdot\text{L}^{-1}$), Q is the flow rate ($\text{L}\cdot\text{h}^{-1}$), m is the adsorbent mass (g), $C(t)$ is the caffeine concentration at time t ($\text{mmol}\cdot\text{L}^{-1}$), t_b is the breakthrough time (h), t_e is the exhaustion time (h), h_{MTZ} is the mass transfer zone height (cm), H_b is the bed height (cm), REM_b is the percentage of caffeine removed up to the bed's breakthrough point (%), and REM_e is the percentage of caffeine removed up to the bed's exhaustion (%).

Breakthrough time was defined as the required time for the caffeine concentration in the outlet to reach 5% of the inlet fluid concentration.²⁶

The mathematical models of Thomas,²⁷ Yoon and Nelson,²⁸ and modified dose–response²⁹ were adjusted to the experimental data, using nonlinear regression, according to eqs 6, 7, and 8, respectively.

$$\frac{C(t)}{C_0} = \frac{1}{1 + \exp\left(\frac{K_{\text{Th}}}{Q}(q_{\text{Th}}m - C_0Qt)\right)} \quad (6)$$

$$\frac{C(t)}{C_0} = \frac{1}{1 + \exp(K_{\text{YN}}(t^* - t))} \quad (7)$$

$$\frac{C(t)}{C_0} = 1 - \frac{1}{1 + \left(\frac{C_0Qt}{q_Y m}\right)^a} \quad (8)$$

where $C(t)$ is the caffeine outlet concentration at time t ($\text{mmol}\cdot\text{L}^{-1}$), C_0 is the adsorbate initial concentration ($\text{mmol}\cdot\text{L}^{-1}$), t is the time (h), K_{Th} is the rate constant of adsorption for Thomas model ($\text{L}\cdot\text{mmol}^{-1}\cdot\text{h}^{-1}$), Q is the flow rate ($\text{L}\cdot\text{h}^{-1}$), q_{Th} is the maximum solid-phase solute concentration estimated by Thomas model ($\text{mmol}\cdot\text{g}^{-1}$), m is the adsorbent mass (g), K_{YN} is rate velocity constant (h^{-1}), t^* is the time required for 50% of the exhaustion (h), a is a constant of the modified dose–response model, and q_Y is the maximum adsorption capacity estimated by the modified dose–response model ($\text{mmol}\cdot\text{g}^{-1}$).

The highest values of the coefficient of determination (R^2) and lowest of the corrected Akaike information criteria (AICc) indicated the best correlations.³⁰ The methodology used in the calculations of R^2 (eq S1) and AICc (eq S2) is presented in the Supporting Information.

3. RESULTS AND DISCUSSION

Clay Characterization. Figure 1 shows thermal analysis curves obtained for the CVL and the CVL contaminated with caffeine (CVL+CAF). The TG curves show a weight loss of 7% for the CVL sample and of 13% for the CVL+CAF during the heating. The higher weight loss of the CVL+CAF sample occurred due to the presence of caffeine. The low weight loss of the CVL sample shows that the modified clay is thermally stable. The DTG curves indicate the temperature range in which there was a larger weight loss for the samples. The bands at 67 °C for the CVL and at 70 °C for the CVL+CAF refer to the presence of water in the material, which was higher for the CVL+CAF possibly due to the presence of adsorbed water in the adsorptive sites of the clay. The verified oscillations in the curves for temperatures above 800 °C can be attributed to the melting, decomposition, and crystallization of minerals present in the bentonite material.³¹ Finally, the DTA curve presented endothermic peaks for the clays with and without caffeine at 75 and 79 °C, respectively, also referring to the loss of water.³² For all curves, the main differences between the two clays were evidenced in the region between 200 and 400 °C, in which caffeine decomposition occurred.³³

Also in Figure 1, the decomposition of caffeine at temperatures about 400 °C without the occurrence of damages to the CVL structure was verified, which suggests the possibility of using thermal regeneration in order to recover the bentonite and reuse it in adsorption processes. Although the use of this technology is possible, the cost of thermal regeneration is more expensive than the cost of new adsorbent, which does not make the recovery of the adsorbent an economically viable process. The use of solvents to regenerate the adsorbent can generate effluents more toxic than the effluents treated by adsorption.

The study of the adsorbent regeneration is mightily connected to the need to improve the economic feasibility of the process. When using a traditional adsorbent, such as activated carbon or granular activated carbon, the recovery of

these adsorbents is important due to the high cost of these materials.³⁴ As occurs with powdered activated carbon, low-cost adsorbents are not usually regenerated, but disposed by landfill or incineration and replaced by fresh materials.³⁵ Nevertheless, the use of a clay material instead of an activated carbon relies on the cost of both materials. While bentonite has an average cost of US\$ 0.072/kg, a commercial activated carbon can reach US\$ 22/kg, which makes the use of the nonconventional adsorbent more profitable.¹

Figure 2 shows the X-ray diffraction spectra for the CVL bentonite without and with adsorbed caffeine.

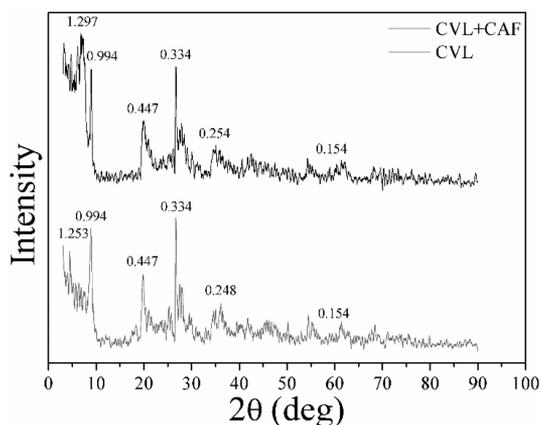


Figure 2. XRD analysis spectra obtained for CVL (angle of incidence from 3 to 90°, 40 kV, 40 mA, step size = 0.02°, velocity = 0.02°·s⁻¹).

According to Figure 2, there was no change in the spectra due to adsorption, since the identified peaks refer to similar interplanar distances. This indicates that the adsorption does not alter the lamellar layers of the crystalline structure of the solid. The peak corresponding to the interplanar distance $d(0.001)$ is 1.297 nm for the CVL sample and 1.253 nm for the clay after adsorption (CVL+CAF). These values are close to the 1.5 nm expected for a bentonite clay,³⁶ and those identified experimentally for montmorillonites.^{37,38} The 0.477 and 0.334 nm peaks, identified for the two clays, happens due the presence of quartz in the material composition.^{39,40} The peaks of 0.994 nm and those close to 0.25 nm were also identified for the CVL in previous studies.^{21,22,41}

Figure 3 combines Fourier transformed infrared spectroscopy (FT-IR) spectra for anhydrous caffeine (CAF) and for modified bentonite before (CVL) and after (CVL+CAF) the adsorption of caffeine.

The spectra of CVL and CVL+CAF, shown in Figure 3, are very similar, differing in a few peaks related to the presence of caffeine in the CVL+CAF sample. The similarity between the spectra of CVL and CVL+CAF is a consequence of the disappearance of peaks related to the presence of caffeine. This indicates a possible predominance of the phenomenon of chemisorption, which causes the adsorbate (caffeine) to bind with the adsorbent (clay) and change the structure of its chemical bonds.

The spectra show peaks at 3112 and 2954 cm⁻¹ for caffeine, which refers to single and double bonded carbon, and at 745 cm⁻¹, which strongly indicates the presence of double bonded carbon hydrogens.^{42,43} The other two characteristic caffeine bands at 1659 and 1701 cm⁻¹ for CAF and 1651 and 1698 cm⁻¹ for CVL+CAF were observed, which can be attributed to the presence of the C=O bond. Besides the presence of CAF

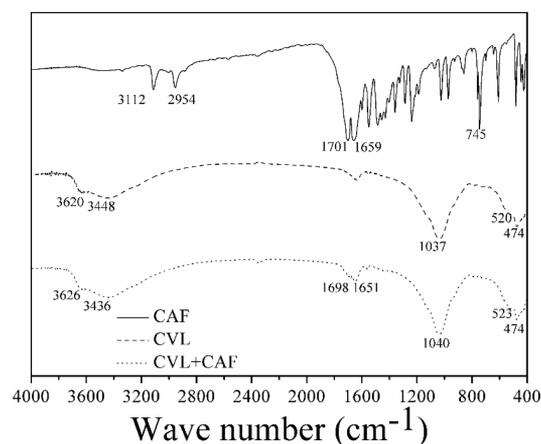


Figure 3. FT-IR spectroscopies for pure caffeine, and for CVL before and after caffeine adsorption (wavelengths in the range of 4000 to 400 cm⁻¹).

in the sample, the peaks at 1698 and 1651 cm⁻¹ can also be associated with the combination of CAF bands with water deformation bands.^{19,44} The presence of water in the samples was also verified in the thermal analysis.

Table 2 summarizes the main observations related to the FT-IR analysis and identifies the corresponding functional groups according to the literature.

Table 2. Functional Groups Related to the Main Peaks Found in the FT-IR of CVL and CVL+CAF Samples

peak before adsorption (cm ⁻¹)	peak after adsorption (cm ⁻¹)	corresponding functional group	ref
3620	3626	O–H stretch (montmorillonite)	Holtzer et al. ⁴⁵
3448	3436	O–H stretch (montmorillonite)	Skoog et al. ⁴²
	1698	C=O (caffeine)	Skoog et al. ^{42,46}
	1651	C=C (caffeine)	Skoog et al. ^{42,46}
1037	1040	Si–O stretch (montmorillonite)	Holtzer et al. ⁴⁵
520	523	Vibrations of Si–O–Si and Si–O–Al groups (montmorillonite)	Karakassides ⁴⁷
474	474	Vibrations of Si–O–Si and Si–O–Al groups (montmorillonite)	Karakassides ⁴⁷

The peaks indicated in Figure 3 and Table 2 confirm the presence of montmorillonite in the CVL structure. This mineral is responsible for the adsorptive properties of the clay material.⁴⁸ Especially for caffeine adsorption, calcined montmorillonite is capable of uptake of this pharmaceutical compound on its surface and intercalate it into its layers.⁴⁹

Figure 4 shows the micrographs obtained for CVL before and after caffeine adsorption. Before adsorption, the porous and irregular structure of the bentonite is easily observed. After adsorption, the clay lost its roughness, possible due to the fill of its pores with caffeine and water, which was also verified in the thermal and FT-IR analyses.

Fixed-Bed Adsorption. Figure 5 shows the obtained breakthrough curves. The average deviations of the experimental curves were below 0.28%. The study varying the flow operating rate, in Figure 5a, showed that the rate of 5 mL·min⁻¹ resulted in the lowest breakthrough and exhaustion

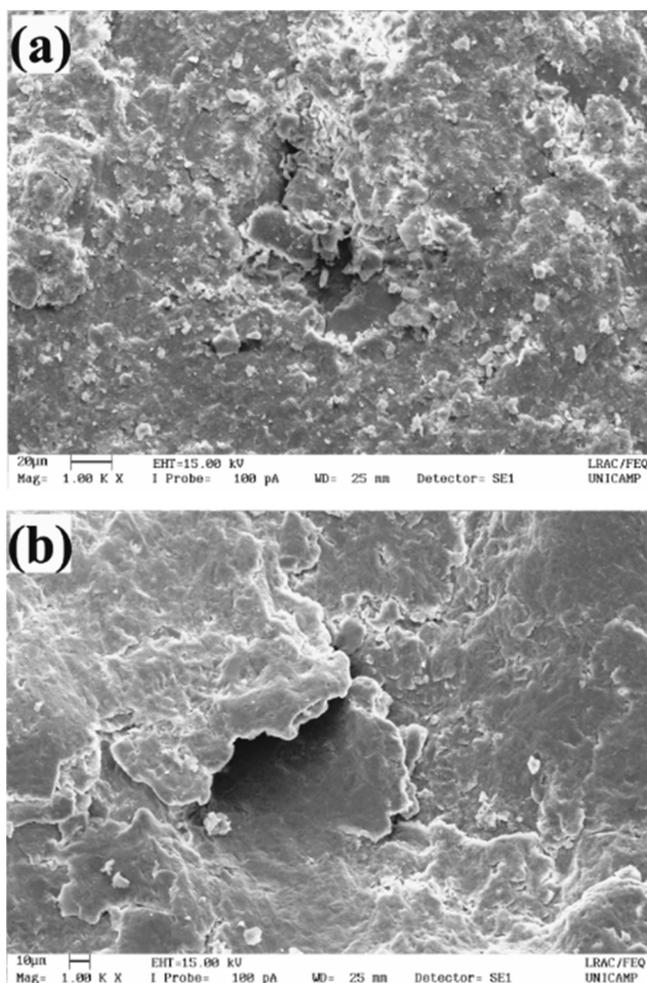


Figure 4. Micrographs with zoom of 1000 \times obtained for CVL before (a) and after (b) caffeine adsorption.

times, followed by 3 mL \cdot min $^{-1}$ and 1 mL \cdot min $^{-1}$, respectively. Higher flow rates make the residence time in the bed insufficient to promote enough contact between the CVL and the caffeine, which leads to a decrease in the removal efficiency.⁵⁰ Considering the observed result, along with the calculated bed efficiency parameters shown in Table 3, the flow rate of 1 mL \cdot min $^{-1}$ was selected to continue the studies varying caffeine inlet concentration. Figure 5b shows that, for a constant flow, the lower is the concentration, the longer are the breakthrough and exhaustion times.

Table 3 shows that for the studies conducted using inlet concentration of 1 mmol \cdot L $^{-1}$ (194.19 mg \cdot L $^{-1}$), larger values of q_u (0.122 mmol \cdot g $^{-1}$ or 23.69 mg \cdot g $^{-1}$) and q_t (0.219 mmol \cdot g $^{-1}$ or 42.53 mg \cdot g $^{-1}$) were obtained for the rate flow of 1 mL \cdot min $^{-1}$, as well as the lowest value of h_{MTZ} (6.19 cm), associated with system ideality. For constant flow, the lowest value of h_{MTZ} (6.05 cm) and highest breakthrough and exhaustion times (150.70 and 237.66 h, respectively) were obtained for the inlet concentration of 0.2 mmol \cdot L $^{-1}$ (38.84 mg \cdot L $^{-1}$).

All the values of h_{MTZ} obtained are still too high to consider the studied systems close to ideal, which indicates that there is a probable resistance to mass transfer in the system, due to diffusional problems caused by the structure of the adsorbent. However, considering that the system was able to operate for over 150 h guaranteeing a removal of almost 100%, the CVL

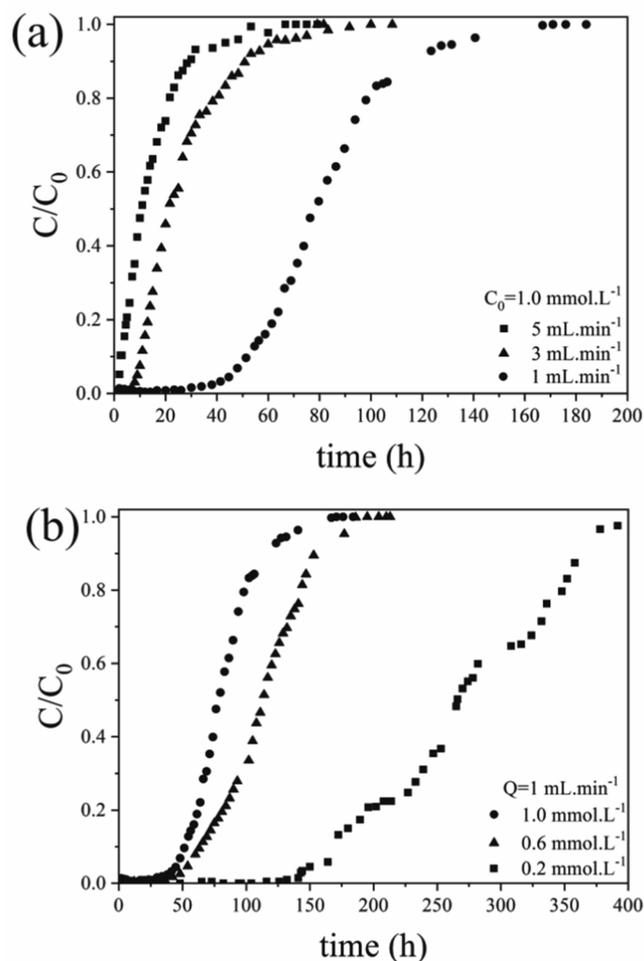


Figure 5. Breakthrough curves for fixed-bed caffeine adsorption varying (a) flow rate at $C_0 = 1.0$ mmol \cdot L $^{-1}$ and (b) inlet concentration at $Q = 0.4$ mL \cdot min $^{-1}$.

can be considered a proper material to be investigated for practical application in real systems.²⁶

The models of Thomas, Yoon and Nelson, and Modified dose–response were adjusted to the experimental data of the five obtained breakthrough curves. Figure 6 shows the adjustment curves obtained for the flow rate of 1 mL \cdot min $^{-1}$ and inlet concentration of 1.0 mmol \cdot L $^{-1}$ (194.19 mg \cdot L $^{-1}$). Table 4 summarizes the calculated parameters for all experimental data.

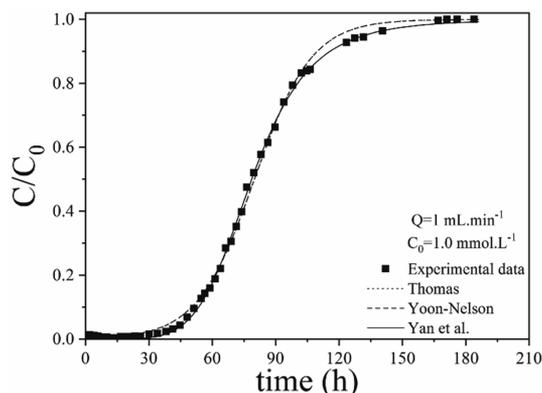
The parameters R^2 and AICc for Thomas and Yoon and Nelson models, shown in Table 4, are equal for all the five cases studied and, according to Figure 6 and Figure S1 from the Supporting Information, the curves referring to the adjustments are overlapping. This can be justified because the two models can be written in the generic form of eq 9.

$$\frac{C(t)}{C_0} = \frac{1}{1 + \exp(a + bt)} \quad (9)$$

The mathematical equivalence between the two models has already been verified in the literature.⁵¹ The basic difference between the Thomas and Yoon and Nelson models is that the second does not require prior knowledge of any operational parameters beyond the $\frac{C(t)}{C_0}$ values, while for the first adjustment to occur, it is necessary to know the values of

Table 3. Adsorption Parameters Obtained in the Fixed-Bed Adsorption Studies

Q (mL·min ⁻¹)	C ₀ (mmol·L ⁻¹)	t _r (h)	t* (h)	t _e (h)	q _u (mmol·g ⁻¹)	q _t (mmol·g ⁻¹)	h _{MTZ} (cm)	REM _b (%)	REM _e (%)
5	1.0	1.99	8.40	50.83	0.026	0.196	12.14	99.9	29.0
3	1.0	9.01	17.98	81.67	0.069	0.209	9.36	98.7	32.8
1	1.0	45.61	70.79	171.00	0.122	0.219	6.19	100.0	47.9
1	0.6	54.60	97.56	186.32	0.087	0.188	7.51	95.2	59.5
1	0.2	150.70	237.66	408.33	0.086	0.152	6.05	100.0	66.1

Figure 6. Adjustments of the mathematical models for breakthrough curve obtained at 1 mL·min⁻¹ and 1.0 mmol·L⁻¹.

operating flow, adsorbent mass in bed, and concentration of solute feed.⁵² The parameters calculated for each model, however, will have different physical meanings.

It was verified in the literature, for some works about adsorption of organic compounds in a fixed-bed system, that there are cases in which the values of R^2 are different between the two models. This difference is due to the use of linear adjustments^{50,53} instead of the nonlinear, as the used in this work. There are also cases with nonlinear adjustments, but values of R^2 still different between the models.^{54,55} In these cases, the eq 7 showed a different arrangement, with a term in the denominator equal to $C_0 - C(t)$, which can lead to a division per zero. This inconsistency may lead the adjustments to be made over different sets of points, resulting in different values of R^2 .

Table 4 also indicates that both the rate constant of adsorption of the Thomas model (K_{Th}) and the maximum

solid-phase solute concentration estimated by the Thomas model (q_{Th}) presented a linear relation ($R^2 > 0.99$) with the flow rate of operation of the bed. The values of K_{Th} increased as a function of the increase in flow and those of q_{Th} decreased. For the cases of inlet concentration variation, it was verified that the higher the concentration of the solution fed to the bed, the lower the values of K_{Th} and those of q_{Th} . This fact can be justified because the higher is the operating flow or the lower the concentration, the lower is the driving force related to the mass transfer from the fluid to the adsorbent particles.⁵⁶

The calculated values of the rate velocity constant of the Yoon and Nelson model (K_{YN}) reflect the behavior of the breakthrough curves shown in Figure 5. The lower is the value of K_{YN} , the longer is the time for bed breakthrough and exhaustion. The times for the 50% saturation (t^*) calculated by the model, shown in Table 4, were very close to the experimental values, shown in Table 3.

The modified dose–response model showed a better fit (higher values of R^2 and lower values of AICc) compared to the Thomas and Yoon and Nelson models for all the three experiments with inlet concentration of 1.0 mmol·L⁻¹ and also a good fit for the experiments with inlet concentrations of 0.6 and 0.2 mmol·L⁻¹. The model fulfilled the purpose of describing the initial data better than the other models,²⁹ but it describes the final points less satisfactorily. For this reason, the values of q_Y are slightly more divergent of the experimental values of q_t (Table 3) if compared to the values of q_{Th} .

Besides this work, there are only two other studies^{14,18} published in the literature about adsorption of caffeine in a fixed-bed system. Table S1, in the Supporting Information, presents the data found and that obtained in this work.

Besides this study, the other two cited works^{14,18} used beds of different dimensions and operated at different flow rates and concentrations. Even at different experimental conditions, the

Table 4. Efficiency Parameters for Caffeine Adsorption onto CVL

model	parameter	Q (mL·min ⁻¹)				
		5		3		1
		C ₀ (mmol·L ⁻¹)				
		1.0	1.0	1.0	0.6	0.2
Thomas	K_{Th} (L·mmol ⁻¹ ·h ⁻¹)	0.2015	0.1276	0.0744	0.0744	0.0988
	q_{Th} (mmol·g ⁻¹)	0.164	0.189	0.214	0.192	0.154
	R^2	0.975	0.977	0.998	0.998	0.990
	AICc	-234.079	-245.655	-372.098	-381.733	-332.327
Yoon and Nelson	K_{YN} (h ⁻¹)	0.1998	0.1260	0.0739	0.0469	0.0212
	t^* (h)	12.31	23.85	79.92	112.95	272.83
	R^2	0.975	0.977	0.998	0.998	0.990
	AICc	-234.079	-245.655	-372.098	-381.733	-332.327
Modified dose–response	a	1.9403	2.7024	5.6947	5.1004	5.5145
	q_Y (mmol·g ⁻¹)	0.141	0.172	0.210	0.188	0.151
	R^2	0.997	0.997	0.999	0.993	0.988
	AICc	-328.273	-341.824	-414.732	-314.554	-326.273

analysis of Table S1 allows observing, by the values of h_{MTZ} for the system of adsorption by CVL, bentonite is more discrepant from ideality when compared to a system that uses carbon-based adsorbents. Even so, the adsorption capacities of the bed (q_u) with clay, calculated in this work, were lower but comparable to the ones using carbon-based adsorbents, which varied between 0.646 and 0.885 mmol·g⁻¹ (125.45 and 171.86 mg·g⁻¹), if the fact that carbon materials can cost more than 300 times more than bentonite.¹ This indicates that the adsorbent used in this work can be considered a material with potential to be employed in future studies.

In the future, studies regarding caffeine adsorption onto CVL may evaluate lower inlet caffeine concentrations, in order to make the synthetic systems more similar to the real ones (superficial waters), and considering that high removal percentages were obtained for over 150 h of contact between the caffeine solution and the clay. Adsorption using CVL may also be applied to multicomponent solutions, with different pharmaceuticals, along with caffeine, since CVL has taken a further favorable step toward its use as an adsorbent of pharmaceutical compounds.

4. CONCLUSIONS

The characterization analysis pointed to the presence of caffeine in the CVL after the contact between them. Thermal analysis showed the decomposition of caffeine around 400 °C and the thermal stability of the clay until 1000 °C. The CVL +CAF XRD showed peaks associated with the montmorillonite, material that composes the CVL. The FT-IR analysis pointed to peaks related to the functional groups of caffeine and montmorillonites and indicated that the predominant adsorption phenomenon is possibly chemisorption. Adsorption studies varied the flow rate and the inlet caffeine concentration and the models of Thomas, Yoon and Nelson, and modified dose–response were well adjusted to all experimental data. The higher breakthrough time was 150.70 h, obtained at 1 mL·min⁻¹ and 0.2 mmol·L⁻¹ and the higher breakthrough adsorption capacity was 0.219 mmol·g⁻¹ (42.53 mg·g⁻¹), obtained at 1 mL·min⁻¹ and 1.0 mmol·L⁻¹. The studied systems removed up to about 100% of the caffeine fed to the bed, indicating the potential of CVL to be used for caffeine uptake from wastewaters.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.8b03734.

Materials and methods; results of caffeine fixed-bed adsorption studies (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Brasil

(CAPES), Finance Code 001. The authors also thanks CNPq for financial support, FAPESP [Proc. 2016/05007-1], Dolomil Industrial Ltda. for the donation of the clay, and MagisPharma for the donation of the caffeine.

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