

ACTIVATION OF TERMITE FECES WITH DIFFERENT CHEMICAL REAGENTS AND THEIR EFFECTS ON NORFLOXACIN ADSORPTION PROPERTIES**ATIVAÇÃO DE FEZES DE CUPIM COM DIFERENTES REAGENTES QUÍMICOS E SEUS EFEITOS NAS PROPRIEDADES DE ADSORÇÃO DE NORFLOXACINA**

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Resumo

Os antibióticos são substâncias classificadas como contaminantes emergentes e são uma preocupação constante devido aos efeitos deletério, ao meio ambiente e ao ser humano, principalmente pelo desenvolvimento de microrganismos resistentes aos antibióticos. A tecnologia atual de tratamento de águas residuais não pode remover antibióticos de esgoto de maneira eficiente e, portanto, novas tecnologias de baixo custo são necessárias. Neste trabalho, foi utilizado um material carbonáceo, preparado com fezes de cupim quimicamente ativado, como adsorvente de baixo custo, para remoção do antibiotico norfloxacina (NOR) presente em meio aquoso. As fezes de cupins foram tratadas com Na₂CO₃ H₃PO₄ e NaOH, 1 M, 24 h e 100 ° C para ativação química e depois lavadas com água destilada. Os experimentos forma feitos em sistema de batelada, para estudar a influência do tipo de adsorvente, pH, tempo de contato, temperatura e concentração inicial de NOR. Para o estudo de sorção, vários parâmetros foram otimizados (pH, temperatura, tempo de contato) e os dados foram ajustados às isotermas de Langmuir, Freundlich e Sips para demonstrar o mecanismo de sorção. Os dados cinéticos foram analisados por equações de pseudo-primeira ordem e pseudo-segunda ordem. Os adsorventes têm uma área de superfície específica entre 61 e 2433 m²/g e um ponto de carga zero entre 7,4 e 10,1, dependendo do agente ativante. O melhor ajuste para as isotermas Sips sugeriu um modelo de adsorção do tipo monocamada, e a capacidade máxima de adsorção do adsorvente foi de 111 mg/g para o adsorvente preparado com fezes de cupim ativada com H₃PO₄ (TFPO₄) e 169 mg/g para o para o adsorvente preparado com fezes de cupim ativada com NaOH (TFOH). Os resultados indicam que o modelo de pseudo-segunda ordem explica a cinética de adsorção de forma mais eficaz, com r² na faixa de 0,961 e 999. Os resultados apresentados neste trabalho mostraram que o que os materiais carbonáceos, quimicamente ativados, como adsorventes de baixo custo, para a remoção da norfloxacina presente em sistemas aquosos.

Palavras-chave: Adsorvente de baixo custo. Material carbonáceo. Antibióticos.

Abstract

Antibiotics are classified as emerging contaminants and they are a constant concern due to their deleterious effects on the environment and humans, mainly due to the development of antibiotic-resistant microorganisms. Current wastewater treatment technology cannot efficiently remove antibiotics from sewage and therefore new, low-cost technologies are needed. In this work, a

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carbonaceous material, prepared with chemically activated termite feces, was used as a low-cost adsorbent to remove the antibiotic norfloxacin (NOR) present in an aqueous medium. Termite feces were treated with 1 M Na₂CO₃, H₃PO₄ and NaOH for 24 hours at 100 °C for chemical activation and then washed with distilled water. Batch experiments were performed to study the influence of adsorbent type, pH, contact time, temperature, and initial NOR concentration. For the sorption study, various parameters were optimized (pH, temperature, contact time) and the data was adjusted to the Langmuir, Freundlich and Sips isotherms to demonstrate the mechanism of sorption. The kinetics data were analyzed by pseudo-first order and pseudo-second order equations. Adsorbents have a specific surface area between 61 and 2433 m²/g and a zero charge point between 7.4 and 10.1, depending on the chemical modifying agent. The best fit for the Sips isotherms suggested a monolayer-type adsorption model, and the maximum adsorption capacity of adsorbent was found to be 111 mg/g for the adsorbent prepared with termite feces activated with H₃PO₄ (TFPO₄) and 169 mg/g for the adsorbent prepared with termite feces activated with NaOH (TFOH). The results indicate that the pseudo-second-order model explains the adsorption kinetics most effectively, with r² between 0.961 and 0.999. The results presented in this work show the potential application of carbonaceous materials as a low-cost adsorbent for the removal of norfloxacin present in aqueous systems.

Keywords: Low cost adsorbent. Carbonaceous material. Antibiotics.

1. INTRODUCTION

Emerging contaminants (EC) are consumed in large amounts every day. The main characteristic of this group of contaminants is that they do not need to be persistent in the environment to order to cause negative impacts; they are replaced in the water as quickly as they can be removed or transformed. But their presence in water resources, and consequently in drinking water, is harmful as they can act as endocrine disruptors in humans and in aquatic organisms (GOGOI et al., 2018; TRAN et al 2018; NILSEN et al., 2019).

Antibiotics can be classified by their chemical structure, such as β -lactams, fluoroquinolones, lincosamides, macrolides, reductase inhibitor, tetracycline, glycopeptide and amphenicol. Antibiotics have recently been recognized as a new class of water EC concern due to their adverse effects on aquatic ecosystems. Residues of veterinary and human antibiotics have been recently detected in in the aqueous system (e.g., municipal wastewater treatment (SENTA et al., 2019), hospital effluents (AYDIN et al., 2019), pharmaceutical manufacture (THAI et al 2028, drinking water (SANGANYADO et al 2019), groundwater (BOY-ROURA et al., 2019) and surface water (DANNER et al 2029),

There are many methods for removing antibiotics: bioreactor membrane processes (LEE et al.,2018), filtration processes (SLIPKO et al., 2019), advanced oxidation processes (Fenton, ozonization, photocatalysis) adsorption processes (MICHAEL-KORDATOU et al 2018). However, adsorption is one of the most common methods because it is simple, efficient, environmentally friendly, and easy to operate and expand on an industrial scale (RASHID et al., 2021).

Activated carbon has long been used as an adsorbent for water purification. The search for low-cost adsorbents, especially biomass residues from agricultural activities, has not been the subject of constant studies. (DE ANDRADE et al 2018; XIANG et al. 2019; FENG et al 2019).

Low-cost biomass wastes are interesting because they are abundant in nature, available in large quantities, inexpensive, and may have potential as adsorbent materials due to their



physicochemical characteristics and particular structure (CRINI et al 2019). Agricultural waste mainly consists of cellulose, lignin and hemicellulose. The content of these chemical components depends on the type of waste that gave rise to them. Cellulose is formed by β - (1 \rightarrow 4)-glycoside bonds, hemicellulose is composed of a variety of uronic acid groups, and lignin is a cross-linked aromatic polymeric compound that consists of p-coumaryl alcohol, coniferyl alcohol and synaphyl alcohol (MO et al 2018; GE, and LI 2018).

Termites consume 3 to 7 billion tons of lignocellulosic materials annually, representing one of the most prolific and efficient lignocellulose decomposers on earth (TARMADI et al., 2018). Termite feces contain about 68% lignin and can be an abundant source of biomass for use as a low cost adsorbent (KATSUMATA et al., 2007). Was recently shown the use of chemically modified termite feces with H₂SO₄ or Fe₃O₄ for the adsorption of norfloxacin and Cr(VI) ions (CHAHM, et al., 2019; DEMARCHI, et al 2019).

Chemical activation is used to improve the adsorption capacity of biomass waste. The purpose of chemical treatment is to break down the bonds between functional groups and the adsorbent surface. These treatments can significantly alter the surface properties and pore structure, which is closely related to the uptake of pollutant molecules (SAHU et al. 2020; ZHANG et al 2020).

Phosphoric acid (H₃PO₄) is considered the most environmentally friendly reagent when compared to other acids, such as H₂SO₄. It promotes the depolymerization of cellulose, dehydration of biopolymers, and formation of aromatic rings, enabling the surface area of the adsorbents to be increased (WONG et al., 2018). Sodium hydroxide (NaOH) and sodium carbonate (Na₂CO₃) are also frequent reagents used in chemical activation. In general, the use of these two reagents results in adsorbents with large specific surface areas (SAYGILI; SAYGILI 2019). The KOH activation process causes more significant destruction of the biomass particle structure, promoting a more homogeneous particle size distribution of the material (LUO et al 2018).

The objective of this work was the preparation of carbonaceous material, using termite feces in less drastic conditions than those reported in the literature (CHAHM et al 2019). The termite feces were chemically activated with diluted solutions of NaOH, Na₂CO₃ and H₃PO₄, and later used to remove norfloxacin present in aqueous medium. Batch adsorption experiments were conducted to evaluate the adsorption process over a wide range of operating conditions (drug concentration, pH, contact time, and temperature). In addition, the kinetics and thermodynamic parameters of the adsorption process were studied.

2. MATERIAL AND METHODS

2.1 Adsorbent material

The termite feces (TF) of *Cryptotermes brevis* fed with *Pinus sp.* were collected at the Biopolymers Laboratory of the Universidade do Vale do Itajaí. The TF were washed with distilled water for 24 h to remove contaminants. Afterwards, FT was dried in oven at 105 °C for 24 h. The dried FT was ground and sieved through a 125 mesh.

2.2 Preparation and characterization of carbonaceous material (CM)



50 g of TF were stirred with 100 mL of 0.250 M of Na_2CO_3 , NaOH or H_3PO_4 for 15 min. Afterwards, the mixture was oven-dried overnight at 100 °C. After activation, the adsorbent was washed using distilled water for removal of excess modifying reagents. Then, the sample was further dried at 100 °C under vacuum for 24 h. The prepared adsorbents were denominated TFCO_3 , TFPO_4 and TFOH .

The point of zero charge (pH_{PZC}) of the adsorbents was determined according to literature (MAHMOOD et al 2017). Briefly, the pH of 20 mL 0.1 M NaCl solution in a closed vessel was adjusted to a range of 3 to 10 with 0.1 M HCl or 0.1 M NaOH . Then, 0.10 g adsorbents were added and the solution pH after 24 h of agitation was measured. The point of zero charge is the point where the curve $\Delta\text{pH} = \text{pH}(\text{final}) - \text{pH}(\text{initial}) = 0$.

The oxygenated acidic groups of the samples were determined using the Boehm's titration (BRUDEY et al., 2016). Sample of adsorbent (0.1 g) was mixed with 20 mL of the 0.05 M solution of NaHCO_3 , Na_2CO_3 , NaOH and HCl . The sample suspensions were shaken at 25 °C for 24 h. The excess base in 5 mL of the filtrate was titrated with 0.05 M HCl or 0.05 M NaOH . Total acidity and the contents of oxygen-containing functional groups were calculated based on the premises that NaHCO_3 neutralizes carboxyl groups only, Na_2CO_3 neutralizes carboxyl and lactonic groups, NaOH neutralizes carboxyl, lactonic, and phenolic groups, and HCl neutralizes basic groups.

The specific surface area (SSA) of the adsorbents was determined using the methylene blue (MB) adsorption method, using a V-630 spectrophotometer (Jasco, Japan). The experiment was conducted by first adding a known mass of adsorbent to a known volume of MB solution of standard concentration. The mixed suspension was stirred continuously for 24 h to reach the adsorption-desorption equilibrium of MB. Suspended materials were removed by centrifuging the mixture. The MB concentration was consequently measured by analyzing the supernatant through UV-Vis spectroscopy at a wavelength of 665 nm compared with the initial standard concentration. The SSA of the aerogel was then calculated using the following equation:

$$SSA = \frac{N_A \times A_{MB} \times (C_0 - C_e) \times V}{M_{MB} \times m_s}$$

where N_A represents Avogadro's constant ($6.02 \times 10^{23} \text{ mol}^{-1}$), A_{MB} represents the area covered per MB molecule (typically $A_{MB} = 1.35 \text{ nm}^2$), C_0 and C_e are the initial and equilibrium concentrations of MB, V is the volume of MB solution, M_{MB} is the relative molecular mass of MB, and m_s is the mass of the sample (KABIR et al., 2014).

2.3 Adsorption experiments

Batch adsorption tests were carried out to investigate the effects of contact time, solution pH, initial NOR concentration and temperature. The pH effect was conducted in 125 mL Erlenmeyer flasks containing 25 mg of adsorbents and 20 mL of NOR solutions (50 mg/L), solution was adjusted (4 and 10) using 0.1 M HCl or 0.1 M NaOH . The suspension was shaken for 24 h at 25 °C. After, the mixture was filtered using a syringe filter, and the remaining NOR in the solution was measured using a V-630 spectrophotometer (Jasco, Japan) at 273 nm.

Equilibrium adsorption experiments were conducted in 125 mL Erlenmeyer flasks containing 25 mg of adsorbents and 20 mL of NOR solutions with different initial concentrations (25, 50, 75, 100, 120 and 150 mg/L). The flasks was shaken for 2 h in a thermostated water bath shaker at 25 °C. After, the mixture was filtered using a syringe filter, and the remaining NOR was determined as described above.



To calculate the thermodynamic parameters, the same steps were followed at different temperatures (25, 35, 45, and 55 °C).

Kinetics experiments were conducted in 125 mL Erlenmeyer flasks containing 25 mg of adsorbents and 20 mL of NOR (50 mg/L) at 25 °C. The flasks were shaken at predetermined time intervals (15, 30, 45, 60, 90 and 120 min). After, the mixture was filtered using a syringe filter, and the remaining NOR was determined as described above.

The Langmuir, Freundlich and Sips isotherm models were used to investigate the adsorption procedure. Kinetic models such as pseudo-first order, pseudo-second order and intraparticle diffusion were used to study the adsorption kinetic mechanisms.

The adsorbed amount of NOR at equilibrium, q_e (mg/g) was calculated using the Equation:

$$q_e = \frac{(C_0 - C_e)V}{M}$$

where C_0 is the initial NOR solution concentration (mg/L); C_e is the equilibrium (residual) NOR concentration (mg/L); V is the volume of NOR solution in each flask (L); and M is the amount of adsorbent (g).

2.3 Adsorption: equilibrium and kinetics

The adsorption equilibrium data for NOR on CMs were evaluated using the nonlinear Langmuir, Freundlich and Sips models, (MURTHY et al., 2019) represented by equations (3), (4) and (5) respectively:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (4)$$

$$q_e = \frac{q_m K_L C_e^n}{1 + K_S C_e^n} \quad (5)$$

where, C_e equilibrium NOR concentration, q_m is the maximum amount of NOR adsorbed in a monolayer (mg g^{-1}), K_L , K_F , K_S , are the adsorption equilibrium constants for each model (L/mg), $((\text{mg/L})^{-1/n})$, (L/mg), respectively, and n is a dimensionless constant.

The Langmuir isotherm is a theoretical model based on the following hypotheses: (i) all the active sites have the same activity, (ii) there is no interaction between the adsorbed molecules, and (iii) the adsorption occurs in a monolayer. The Freundlich isotherm assumes heterogeneity of the surface of the adsorbent, with a non-uniform distribution of enthalpy of adsorption. The Sips isotherm is a combined form of the Langmuir and Freundlich isotherms.

In the present study, the most frequently used nonlinear kinetic models were the pseudo-first order (LIU; LIU 2008), the pseudo-second order (HO; MCKAY 1999) and the diffusion intraparticle model Weber-Rumer (PALURI; DURBHA 2021) represented by Equations (6), (7) and (8) respectively:

$$q_e = q_t + (1 - \exp^{-K_1 t}) \quad (6)$$

$$q_e = \frac{q_e^2 K_2 t}{1 + q_e K_2 t} \quad (7)$$



$$q_e = K_{ip}^{0.5} + C \quad (8)$$

where K_1 , K_2 and K_{ip} are the first and second order kinetics and the intraparticle constant, respectively, and q_t and q_e are the amounts of NOR adsorbed in a time “t” and at the equilibrium, respectively.

3. RESULTS AND DISCUSSION

3.1 Characterization of carbonaceous materials (CM)

The specific surface area (SSA) of the CM was determined by the methylene blue adsorption method and are shown in Table 1. FTOH and FT CO_3 had the highest SSA, compared to TF PO_4 , which showed relatively very low SSA values. The variation in surface area produced might be due to different reagents that were used during the activation process. NaOH reacts with carbon in the precursor to form Na $2CO_3$, which then further reacts with carbon to form Na, Na $2O$, CO and CO 2 . These processes generate porosities in the adsorbents with large micropore volume and narrower size distribution and elevated SSA (ZHANG et al., 2017).

The pH at which the adsorbent surface charge takes a zero value is defined as the point of zero charge (pH $_{pzc}$). The estimation of pH $_{pzc}$ value is an important key parameter for predicting the mechanism of adsorption onto CM, which is mainly influenced by the ionization of functional groups from the adsorbent and their interaction with NOR in the solution. As shown in Table 1, the pH $_{pzc}$ of the pH ranged from 7.4-10.1 depending on the reagent used in the activation. When the acid was used, the pH $_{pzc}$ was 7.4, but when basic reagents were used, the pH was above 7.4. The TF surface is negatively charged and could interact with NOR $^+$ (cationic species), while at pH values lower than pH $_{pzc}$, the solid surface is positively charged and could interact with NOR $^-$ (anionic species) (YANG, et al 2012).

The results of the Boehm titration are shown in Table 1. The number of acidic sites on CMs is significantly higher compared to the number of basic sites, indicating that the oxygenated groups were introduced onto the surface of prepared materials during the activation process.

Table 1: Characterization of carbonaceous materials

Adsorbent	SSA (m 2 /g)	pH $_{pzc}$	AG (mg/g)	LC (mg/g)	PG (mg/g)	TA (mmol/g)	BG (mmol/g)
TF PO_4	61	7.4	6.3	40.61	167.9	2.5	0.5
TFOH	2433	8.9	12.7	47.37	167.8	2.7	0.2
TF CO_3	1957	10.1	10.8	57.53	207.6	3.2	0.6

SSA (specific surface area) AC (acid groups); LC (lactonic groups); PG (phenolic groups); TA (total groups); BG (basic groups); Termite feces modified with H $3PO_4$ (TF PO_4), with NaOH (TFOH), with Na $2CO_3$ (TF CO_3)

3.2 Adsorption norfloxacin

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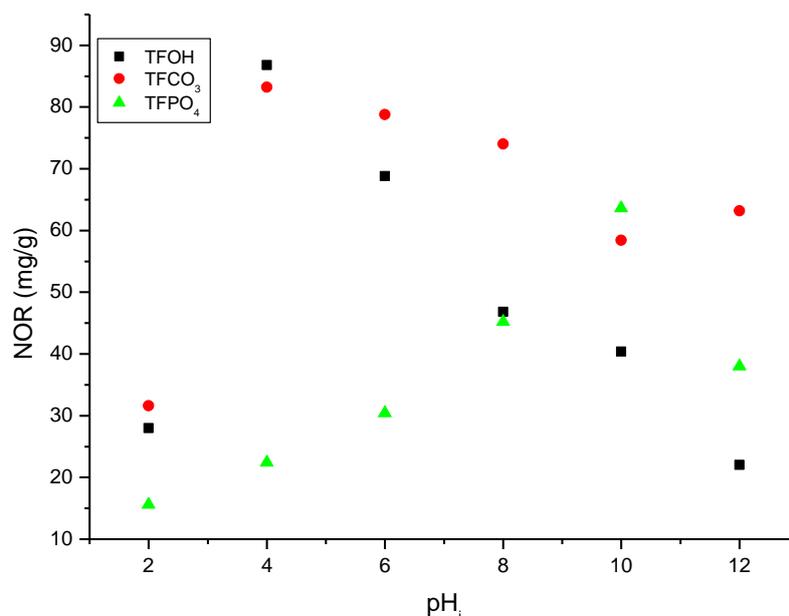
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3.2.1 Effect of pH

The pH plays a critical role in the adsorption of adsorbate by CMs. In general, the pH not only affects the solubility of compounds, but also changes the surface charge characteristics of the adsorbent, thereby changing the interaction between the adsorbent and the compounds. NOR has two proton-binding sites (carboxyl and piperazinyl group) with pK_a values of 6.22 and 8.51, respectively. Therefore, NOR can exist as cationic form NOR^+ , zwitterionic and neutral form NOR^\pm/NOR^0 , or anionic form NOR^- , depending on the solution pH (YANG, et al 2012).

At pH 2, NOR adsorption was < 35 mg/g for all adsorbents. At $pH < 4.0$ NOR is 100% protonated, so the amount of NOR adsorbed is small. This behavior occurs for all adsorbents. In this pH range (2-10), the three surface adsorbents are positively charged, $pH < pH_{pzc}$, resulting in a small adsorption capacity of NOR, Figure 1. However, when the pH was increased to 4, the maximum adsorptions of 83 and 87 mg/g were achieved for $TFCO_3$ and $TFOH$, respectively, which may be attributed to hydrogen bonding between NOR and the adsorbents.

Figure 1: Effect of pH on adsorption of NOR on CMs. Experimental conditions: initial concentration, 50 mg/L; agitation time, 24 h; dosage, 1.25 g/L; and temperature, 25°C.



A similar result was obtained for NOR adsorption in *Moringa oleifera* with optimal pH 5 (WUANA et al., 2016). Adsorption capacity was found to decrease when pH was increased from 4 to 10, except for $FTPO_4$ for which an increase in adsorption was observed. The decrease in the percentage removal of NOR between pH 4 and 10 is noteworthy, and may be due to the zwitterionic or neutral form of NOR^\pm/NOR^0 ($6.0 < pH < 8.5$ 80%). However, there was a considerable decrease in NOR adsorption at pH 12 for TFOH (20 mg/g). At $pH > 11$, the NOR^- is 100%, and leads to a significant decrease in removal efficiency.

The behaviors observed for these adsorbents are different from those reported for termite feces activated with H_2SO_4 in which there is practically no significant change in the adsorbed amount in the pH range of 4 and 10 (CHAHM, et al., 2019).

The adsorption interactions between the CM and NOR can be described as physical adsorption (electrostatic interactions) and chemical adsorption, (Lewis acid-base, van der Waals,

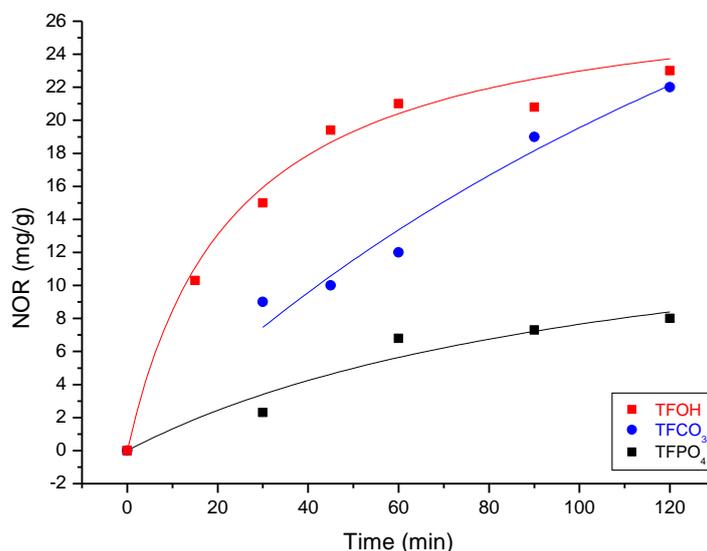
hydrophobic, hydrogen bonding interactions, and π - π interactions). Electrostatic interaction refers to the interaction of a charged CM with an oppositely charged adsorbate, and often occurs in the adsorption process of NOR. Hydrogen bonding and electrostatic attraction through the carboxylic groups and protonated amine of NOR, respectively, seem to play significant roles in the adsorption onto the surface of carbonaceous-like adsorbents. Hydrophobic interactions (type π - π interaction) occur between benzene rings on the adsorbent surface and benzene rings or C=C double bonds of NOR molecules. The hydrogen bonding interaction and van der Waals interactions also played significant roles in the adsorption processes onto CMs. Fluorine groups that bind to benzene rings act as π electron receptors due to the high electron removal capacity of N and F (ROSTAMIAN et al., 2017).

3.2.2 Adsorption kinetics

Adsorption kinetics is expressed as the solute rate that controls the residence time of the adsorbate in the solid-solution interface. The kinetic behaviors of FTOH, FT CO_3 and FT PO_4 toward NOR adsorption were shown in Fig. 2. The NOR adsorption were very rapid in the first 40 min and the adsorption equilibrium was achieved within 90 min.

Three kinetic models were applied to fit the sorption process in this study: pseudo-first order, pseudo-second-order, and the diffusion intraparticle model. In this study, nonlinear regression was used to determine the best-fit kinetic model rate equation. Therefore, in this study, by nonlinear regression plots, goodness of conformity between the experimental data and the model-predicted values was evaluated with emphasis on the correlation coefficient (r^2),

Figure 2: Kinetics of NOR adsorption on CMs by fitting no linearized pseudo-first order model; experimental conditions: Agitation time 60 min; dosage, 1.25 g/L; and temperature, 25°C



The kinetic constants and r^2 , SSR and χ^2 for the kinetic models are listed in Table 2. The r^2 for the pseudo-first-order kinetic model are ≥ 0.957 and calculated q_e values (q_{ec}) from the pseudo-first-order kinetic model agreed with the experimental data ($q_{e,exp}$). This shows that the adsorption process of NOR onto the FTOH and FT PO_4 follows a pseudo-first-order. The applicability of the

pseudo-first order model suggested that the adsorption NOR onto adsorbents could be classified as physisorption.

On the other hand, The r^2 values of the pseudo-second-order kinetic model were higher than 0.997, and the calculated q_{ec} values agreed very well with the experimental data, which indicates that the adsorption process of NOR onto the TFCO₃ follows a pseudo-second-order kinetic model.

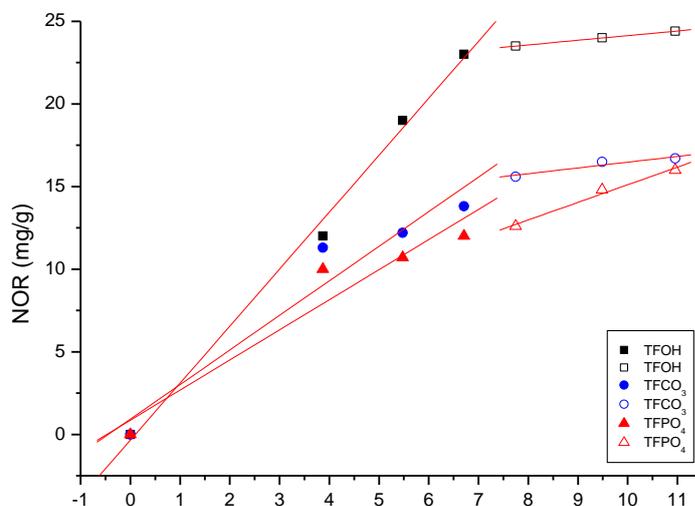
Table 2: Kinetics parameters for norfloxacin adsorption on carbonaceous material

(°C)	Pseudo first-order					Pseudo second-order						
	q_{eex}	q_{ec}	K_1	r^2	X^2	SSR	q_{ec}	K_2	r^2	X^2	SSR	
TFOH												
25	23	29	0.025	0.94	1	19	22	0.039	0.99	0	0	
35	24	24	0.048	0.99	1	17	29	0.0020	0.99	1	3	
40	22	22	0.048	0.98	3	21	22	0.013	0.97	1	5	
55	19	22	0.0028	0.99	2	18	19	0.039	0.99	2	4	
TFCO ₃												
25	22	38	0,0078	0.98	2	6	64	6.8×10^{-5}	0.983	1	5	
35	17	16	0.065	0.98	1	5	18	$5,1 \times 10^{-3}$	0.99	0	2	
40	18	18	0.051	0.99	0	1	22	2.9×10^{-3}	0.92	0	5	
TFPO ₄												
25	28	29	0.025	0.97	4	20	40	5.2×10^{-4}	0.96	5	27	
35	16	14	0.055	0.93	5	19	17	0.0047	0.98	4	21	
40	16	15	0.064	0.98	3	18	17	0.0052	0.99	3	19	
55	25	25	0.0041	0.98	4	18	23	0.073	0.98	5	25	

q_{eex} (mg/g); q_{ec} (mg/g); K_1 (1/min); K_2 (g/mg min); Termite feces modified with H₃PO₄ (TFPO₄), with NaOH (TFOH), with Na₂CO₃(TFCO₃)

The Fig. 3 shows that there were two linear portions, indicating two adsorption stages. The intra-particle diffusion mode was plotted, to determine the influence of mass transfer resistance on the binding of NOR to the CM. Thus, the intra-particle diffusion constant, K_{ip} can be obtained from the slope of the plot of q_t versus the square root of time (S1 and Fig. 3).

Figure 3: Weber-Morris plot of the kinetic data for adsorption of NOR on CMs; experimental conditions: initial concentration, 50 mg/L; agitation time; dosage, 1.25 g/L; and temperature, 25°C.



DOI: <http://dx.doi.org/10.24021/raac.v19i1.6653> Time^{0.5} (min^{0.5})

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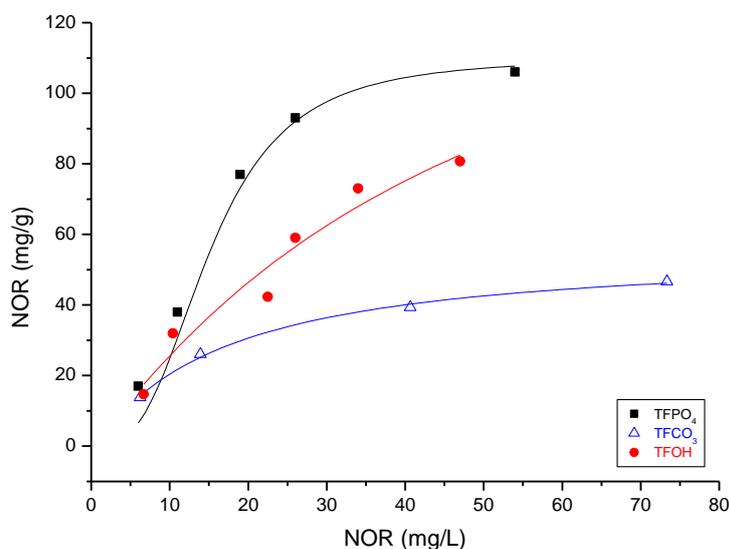
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Table S1 further shows the diffusion parameters (K_{ip} , C) modelled for NOR with the three CMs. The mass transfer of NOR to adsorbents was characterized by both film diffusion (C_1) and intra-particle diffusion (C_2). The higher value of C_2 indicated a thicker boundary layer in relation to intra-particle diffusion, and intra-particle diffusion was the rate-limiting step for the CMs.

3.2.3 Adsorption isotherms

Equilibrium isotherm studies are important to predict the behavior of adsorbate adsorption onto the sorbent surface. Equilibrium data for NOR adsorption onto FTOH, TFPO₄ and TFCO₃ were analyzed using nonlinear regression, and the Langmuir, Freundlich and Sips isotherm models (at different temperatures, Table 4 and Figure 4. These isotherm models were statistically evaluated using three well known goodness-of-fit parameters; the square of the correlation coefficient (r^2), the sum of squares due to regression (SSR), and the Chi square test (χ^2).

Figure 4: Adsorption equilibrium data for NOR adsorption on CMs fitted with Sips model. Temperature 25 °C



The isotherm parameters are summarized in Table 3. In this table, based on the r^2 , χ^2 and SSR, the Sips isotherm model is the best fit compared to the other isotherm models used, as confirmed by the high value of R^2 in the case of Sips (>0.940), which shows that the adsorption of NOR on CMs takes place as monolayer adsorption on a surface that has homogenous adsorption affinity. The q_m Sips constants decreased when the temperature was increased, indicating that the adsorption density was higher at higher temperatures. In addition, it shows that the Sips isotherm gave the maximum adsorption capacity of 169.55 and 111 mg/g for of NOR onto FTOH, TFCO₃ and FTPO₄ respectively, at 25 °C.

Comparing the maximum adsorption capacity of CMs in this work with that of some other adsorbents reported in the literature (Table 4) it can be seen that chemically activated termite feces

were more efficient in adsorbing NOR than most of the low-cost adsorbents listed in the table. All biochar and activated carbons have greater pollutant adsorption capacity when compared to chemically activated adsorbents (PENG et al 2018; QIN et al 2017; QIN et al 2017; FENG et al 2016). However, they are all synthesized, making their production more time and energy consuming and complicated, and requiring the use of many chemical reagents. The production of biochar and activated carbon from agricultural waste is also energy consuming as it requires a pyrolysis temperature >400 °C. These solids have as main characteristic, large surface area and therefore more adsorption site.

Table 3: Isotherm parameters, Sips model, for norfoxacin adsorption on carbonaceous material.

TFPO ₄						
	$q_m(\text{mg/g})$	$K_S (\text{L/g})$	C	r^2	X^2	SSR
25 °C	111	1.9×10^{-3}	2.3	0.992	13	27
35 °C	38	4.4×10^{-7}	4	0.998	1	3
40 °C	42	3.5×10^{-3}	1.1	0.942	2	19
55 °C	43	3.5×10^{-3}	1.1	0.970	8	24
TFCO ₃						
	$q_m(\text{mg/g})$	$K_S (\text{L/g})$	C	r^2	X^2	SSR
25 °C	55	5.4×10^{-2}	2.3	0.996	1	3
35 °C	43	2.4×10^{-2}	4	0.956	4	15
40 °C	66	2.3×10^{-2}	1.1	0.965	7	22
55 °C	154	4.7×10^{-3}	1.1	0.957	10	40
TFOH						
	$q_m(\text{mg/g})$	$K_S (\text{L/g})$	C	r^2	X^2	SSR
25 °C	169	5.5×10^{-2}	2.3	0.953	36	146
35 °C	87	2.9×10^{-2}	4	0.985	5	21
40 °C	77	2.2×10^{-2}	1.1	0.997	2	5
55 °C	118	7.4×10^{-3}	1.1	0.831	50	203

q_m (mg/g); K_L (L/g); K_S (L/g); K_F (L/g); Termite feces modified with H₃PO₄ (TFPO₄), with NaOH (TFOH), with Na₂CO₃(TFCO₃)

On the other hand, some low-cost adsorbents, without any treatment, have a low adsorption capacity, in these cases the adsorption only occurs through the interaction of the drug with the functional groups present in the residue (PAREDES-LAVERDE et al 2018; DUAN et al 2019).

The maximum adsorption capacity of prepared CMs is higher than those previously reported for termite feces chemically activated with H₂SO₄ 32 mg/g (Table 4) (CHAHM, et al., 2019). The main advantage over FTSO₄, in addition to the higher adsorption capacity, is the condition of preparation of this adsorbent (TF:H₂SO₄ 50% m/m), which is more drastic when compared to those used in this work.

3.2.3. Thermodynamic parameters

Thermodynamic parameters such as (J/mol), enthalpy change (ΔH^0) (kJ/mol), free energy change (ΔG^0) and entropy change (ΔS^0) (kJ/ mol K) for the adsorption of adsorbate were calculated through Equations (9)–(11)



$$K_D = \frac{C_s}{C_e} \quad (9)$$

$$\Delta G^0 = -RT \ln K_D \quad (10)$$

$$\ln K_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (11)$$

where, R stands for the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), K_D is the equilibrium constant, C_s is the amount of NOR adsorbed (mg/g) C_e is the NOR equilibrium concentration (mg/L).

The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of van't Hoff plots of $\ln k_d$ versus $1/T$ respectively, Figure 5. The calculated thermodynamic parameters such are given in Table 5. The negative value of ΔH^0 for NOR adsorption at for different temperature (25, 35, 40 and 55 °C) indicates that the adsorption process is exothermic which is similar to the situation discussed in the literature.

Table 4: Comparison of the maximum adsorption capacities of some adsorbents with termite feces chemically modified.

Low-cost adsorbent	adsorption	Ref
potate stem	3.12 (Langmuir)	LI et al., 2017
<i>Moringa olifera</i>	1.88	WUANA et al., 2016
rice husks	20.12 (Langmuir)	PAREDES-LAVERDE et al 2018
	33.56 (Langmuir)	
coffee husks		
bamboo-based activated carbon	173.3 (Langmuir)	PENG et al 2018
biochar of roots cauliflowers	81.30 (Langmuir)	QIN et al 2017
granular activated carbon	112.86 (Langmuir)	
NaClO ₂ -modified <i>calotropis gigantea</i> fiber	68.95 (Langmuir)	DUAN et al 2019
cassava biochar	1.67 (Langmuir)	LUO et al 2018
KOH-modified cassava biochar	5.00 (Langmuir)	
Luffa sponge biochar	278 (Langmuir)	FENG et al 2016
TF ₂ SO ₄	32 (Sips)	CHAHM, et al., 2019
TFOH	169 (Sips)	this work
TF ₂ CO ₃	55 (Sips)	this work
TFPO ₄	111 (Sips)	this work



The negative ΔG^0 values indicated that the NOR adsorption onto the CMs was a spontaneous and favorable process. The decrease in ΔG^0 values with the increase in temperature indicates that the process is more favorable at high temperatures. The negative values of ΔS^0 are attributed to the decrease in freedom degree of adsorbed species at the solid/solution interface. The negative value of ΔH^0 is further indicative of the exothermic process of the adsorption. NOR adsorption onto the CMs was exothermic, and the low ΔH^0 values suggested physisorption.

Figure 5: Van't Hoff plot of $1/T$ against $\ln K_D$ for the adsorption of NOR on CMs at different temperatures.

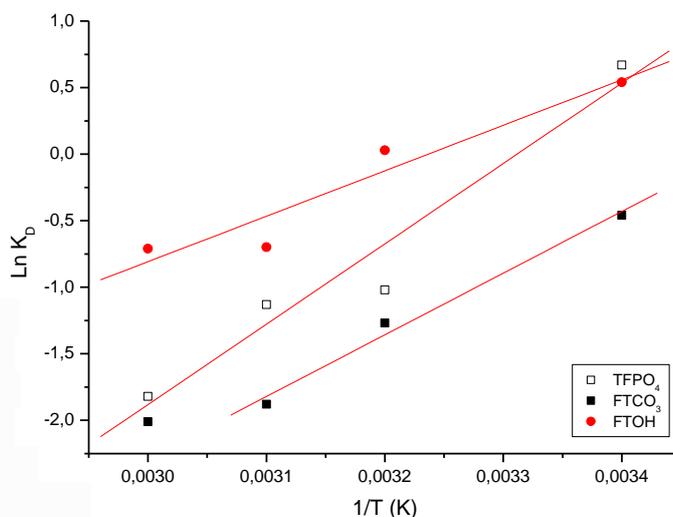


Table 5: Thermodynamic parameters

	ΔS^0	ΔH^0	ΔG^0	r^2
TFPO ₄	-116.3	-50.2	(298) 1.7	0.975
			(308) -2.6	
			(318) -3.0	
			(328) -5.0	
TFCO ₃	-133.0	-38.5	(298) -1.1	0.994
			(308) -3.2	
			(318) -4.9	
			(328) -5.3	
FTOH	-91.4	-28.4	(298) 1.3	0.959
			(308) 0.07	
			(318) -1.0	
			(328) -1.9	

ΔS^0 (J/mol); ΔH^0 (KJ/mol K); ΔG^0 (kJ/mol); Termite feces modified with H₃PO₄ (TFPO₄), with NaOH (FTOH), with Na₂CO₃(TFCO₃)

3.3 Cost Analysis.

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Cost analysis is one of the important parameter for selecting the adsorbent for the removal of contaminants from wastewater. Currently, commercial activated carbon is used as adsorbent in treatment process, but it is costly. Therefore, there is a need for a lost cost adsorbent that is as effective as activated carbon, cheap, and readily available in nature. The present work is based on Na_2CO_3 , NaOH and H_3PO_4 chemically modified termite feces and, following a detailed study of its adsorption capacity and cost analysis, it is found to be the most suitable replacement for activated carbon, and useful for industries. Details of the cost analysis are shown in Table S2. The estimated cost of producing carbonaceous material from termite feces was between US\$ 0.50 and 0.68 per kg, well below the cost of active carbon (US\$ 7.75 per Kg).

4 CONCLUSIONS

Termite feces were chemically modified with sodium hydroxide, sodium carbonate and phosphoric acid. The prepared adsorbent was used to remove norfloxacin from aqueous solution. The adsorption equilibrium data were best described by the Sips isotherm model. The maximum adsorption capacity, calculated from the Sips model, were 169 mg/g, 111 mg/g and 55 mg/g for TFOH, TFPO₄ and TFCO₃ adsorbents, respectively. Kinetic studies showed that NOR adsorption followed the pseudo-first-order model. Thermodynamic studies demonstrated that the adsorption was a physical process and further negative value of ΔG , ΔH and ΔS showed that the adsorption process is a spontaneous, exothermic and random process. The estimated cost of producing carbonaceous materials from termite feces is lower when compared to commercial activated carbon. Based on this study, it can be concluded that adsorbents are a potential adsorbent for the removal of norfloxacin in from wastewater.

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SUPPLEMENTARY MATERIAL

Table S1: Intra-particle diffusion model parameters for adsorption norfloxacin onto carbonaceous material

Temperature (°C)	Step 1			Step 2		
	C ₁	K_{ip} (mg/g min ^{-0.5})	r ²	C ₂	K_{ip} (mg/g min ^{-0.5})	r ²
TFOH						
25	0.28	2.84	0.995	15.2	0.59	0.801
35	0.34	3.34	0.997	21.2	0.28	0.999
40	0.41	2.99	0.996	18.6	0.32	0.957
55	1.07	2.50	0.967	13.5	0.52	0.976
TFPO ₄						
25	2.05	3.01	0.942	12.1	1.4	0.996
35	0.85	1.81	0.965	4.4	1.1	0.993
40	0.68	2.05	0.981	13.3	0.2	0.958
55	1.64	2.95	0.954	9.4	1.4	0.958
TFCO ₃						
25	0.09	1.51	0.996	11.8	3.1	0.984
35	0.92	2.09	0.968	13.0	0.4	0.954
40	0.11	2.55	0.994	14.1	0.4	0.946
55	0.18	2.04	0.965	14.8	0.8	0.968

K_{ip} (mg/g min^{-0.5}); K_{ip} (mg/g min^{-0.5}), Termite feces modified with H₃PO₄ (TFPO₄), with NaOH (TFOH), with Na₂CO₃(TFCO₃)



Table S2; Cost estimation of carbonaceous material production.

Material	Unit cost (R\$)	amount used (g)	TFCO ₃ (R\$)	TFOH (R\$)	THPO ₄ (R\$)	THSO ₄ (R\$)
Na ₂ CO ₃	11.00/Kg	52	0.57			
NaOH	40.00/Kg	20		0.80		
HPO ₄	52.00/Kg	24			1.24	
H ₂ SO ₄	48.00/Kg	500				24.00
termite feces	0/Kg	1000	0	0	0	0
cost of dry/activation (110 °C, 24h)	0.47/KWh	3.6 KW	0.56	0.56	0.56	0.56
cost of washed net cost	44.00/m ³	1.5 L	0.66	0.66	0.66	0.66
other overhead costs (10% of net cost)			1.79	2.02	2.46	25.22
total cost/Kg			0.18	0.20	0.25	2.25
			1.97	2.22	2.71	27.47
			(0.50)*	(0.55)	(0.68)	(6.87)
price commercial activated carbon/Kg						
	31.00 (7.75)					

(values in parentheses represents the price in US \$); Termite feces modified with H₃PO₄ (TFPO₄), with NaOH (TFOH), with Na₂CO₃(TFCO₃) and with H₂SO₄ (TFSO₄) (CHAHM et al 2019).

