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Kinetics and adsorption isotherms of the removal of ibuprofen on a porous adsorbent made from agroindustrial waste

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ABSTRACT

The objective of the present project was to study the kinetics and adsorption isotherms of ibuprofen using a porous carbon-activated type adsorbent at low temperature from cocoa husk impregnated with zinc chloride. In this sense, the precursor was immersed in a $ZnCl_2$ solution at the impregnation ratios 1:2 (CA 1:2) and 1:3 (CA 1:3), for carbonization. Kinetics and adsorption isotherms were performed at three concentrations of contaminant (20, 30 and 40 mg L^{-1}), adjusting to the pseudo-first, pseudo-second-order and Elovich kinetic models and to the isothermal models of Langmuir and Freundlich. It was found that by using initial contaminant concentrations of 20 and 30 mg L^{-1} using the CA 1:2 and CA 1:3, the system tends to reach equilibrium 180 min after the process started, the model of pseudo-first and pseudo-second-order adjusts the experimental data. Additionally, adsorption isotherms were adjusted to the Freundlich model, and from the results, it was established that the adsorption process is controlled by chemical reaction. The maximum adsorption capacity of 123.694 mg g^{-1} was reached using the CA 1:2, the activated carbon from the cocoa husk is recommended to remove ibuprofen present in aqueous solution. A novel porous biomaterial is proposed to be prepared at a low temperature and with a large surface area, which makes it low cost and promising from a low power consumption point of view.

Keywords: Activated carbon; Drugs; Equilibrium; Kinetics; Modelling; *Theobroma cacao*

1. Introduction

Emerging pollutants cover a wide range of artificial chemicals (such as pesticides, cosmetics, personal and household care products, pesticides, hormones, steroids, medications, among others), which do not have regulation for monitoring and treatment of contaminated effluents [1]. Consequently, they have the potential to enter the environment and cause adverse effects on ecosystems and health [2].

Pharmaceutical products are of particular scientific interest, due to the possible toxicological risks and the implications derived from human exposure through drinking water, for example, the development of antibiotic-resistant bacteria, feminization of male fish and toxicity and genotoxicity in aquatic organisms [2,3]. Ibuprofen is one of the most discharged drugs to the environment due to self-medication, hospital discharge, elimination of expired drugs, among other sources of emission [4]. Moreover, its

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presence in the environment is representative because it generates alterations in the endocrine system of aquatic species [5]. This fact implies a clear need to create and develop effective treatments to remove this compound from aquatic environments.

Numerous treatments have been used to eliminate ibuprofen from aqueous solutions, such as electrochemical degradation, UV-degradation, photo-Fenton oxidation, ultrasonic degradation, membrane bioreactor technology, membrane filtration (nanofiltration and reverse osmosis), or degradation by Fe^{2+}/Ozone/UV processes [6]. Bio adsorption is a simple and economical treatment method to eliminate ibuprofen in wastewater, which has led to the search for low-cost materials with a good removal capacity [7].

Many sorbents have been tested for the elimination of ibuprofen; for example, silica nanolayer [8], activated carbon [9], or paper mill sludge-based activated carbon [10]. Activated charcoals made from residues of lignocellulosic origin are widely used in the removal of contaminants due to the availability of the raw material. Coals that have been prepared from potato peel [11], *Schumannianthus dichotomus* [12], Brantii oak [13], functionalized bean husks [14] and green soybeans [15] have shown to eliminate ibuprofen. In this context, the application of modified activated carbon developed from the cocoa husk as an adsorbent is the first attempt reported yet for the elimination of IBP in aqueous solution.

Cocoa (*Theobroma cacao* L.) is a kind of fruit tree from the rainforests of South America. It generates large volumes of waste since only the seed, which is equivalent to 10% of the total mass of the product, is harnessed [16]. The generated waste, shell and pulp, are the focus for the propagation of fungi that cause the decomposition of the fruit, highlighting *Phytophthora palmivora* (Butl.) as the most important pathogen that affects plantations [17,18]. Therefore, the objective of this study was to take advantage of the cocoa shell for the preparation of activated carbon at low temperature and impregnated with zinc chloride ($ZnCl_2$). To assess the kinetics and isotherms of ibuprofen removal using three kinetic models (pseudo-first-order, pseudo-second-order, and Elovich) and two models of sorption isotherms (Langmuir, and Freundlich).

2. Methodology

2.1. Conditioning and preparation of biomass

The cocoa husk was elaborated by reducing the biomass size in order to achieve higher uniformity in the heating. Then, it was washed with deionized water and dried for 48 h at 105°C [19]. Finally, it was ground and sieved at a particle size between 1 and 2 mm.

2.2. Impregnation of carbon with $ZnCl_2$

For the preparation of the coal, 5 g of the pre-treated precursor was impregnated with 15 mL of $ZnCl_2$ solution at concentrations of 1:2 (CA 1:2) and 1:3 (CA 1:3) then, they were placed in the shaker at 50°C, 150 rpm for 3 h. Subsequently, the treated biomass was heated from 150°C to 350°C with a heating rate of 5°C min^{-1} [20]. The carbon type of product obtained was washed with 0.1 M hydrochloric acid. Finally, it was washed with plenty of distilled water and dried at 105°C.

2.3. Adsorption kinetics

Adsorption kinetic study was carried out by contacting the biomass understudy with 100 mL of solution contaminated with ibuprofen at concentrations of 20, 30 and 40 mg L^{-1} with 0.4 g of carbon. Tests were shaken at 120 rpm for 10 to 300 min to know the behavior of the kinetics of metal removal at different concentrations. The contaminant was determined using visible-ultraviolet spectrophotometry (UV-Vis) (Shimadzu model 1700, Pharma Spec, State of Mexico, Mexico) at 220 nm [21].

The data obtained were adjusted to the experimental models using non-linear regression due to a decrease in errors in OriginPro® (OriginLab, Northampton, Massachusetts, EE.UU), with the sum of squares (SS) as adjustment criteria. Kinetic experiments indicate the necessary extent to reach the equilibrium condition, and those of adsorption isotherms establish the distribution of metal ions in the liquid and solid phase in the equilibrium. Thus, experimental kinetics data were fitted to the pseudo-first, pseudo-second-order and Elovich models, and those from isotherms to the Langmuir and Freundlich models, which are shown in Table 1.

3. Discussion

3.1. Adsorption kinetics

The kinetic study was carried out to analyze the behavior of the adsorption process over time. In Fig. 1, the kinetic curve and the fit were made for the adsorption of ibuprofen using the adsorbent at 1:2 impregnation ratios (CA 1:2) are presented.

From the experimental data, it is observed that the adsorption process reached the equilibrium at 180 min at concentrations of 20 and 30 mg L^{-1}; however, at 40 mg L^{-1}, it is observed that the process slower, reaching equilibrium at 200 min. After this time, the process began to stabilize. This behavior is an indicator that the available sites in the adsorbent begin to saturate and therefore, the capacity does not change significantly over time [22]. The fit between the laboratory results and the standard parameters applied was compared with the correlation coefficients.

From the graphs in Fig. 1 and the data reported in Table 2, it can be inferred that the pseudo-first-order model is the one that presents a better fit to experimental adsorption data of ibuprofen at 20 and 30 mg L^{-1}. On the other hand, the Elovich model is the one that describes better the behavior of the experimental data for the initial adsorbate concentration of 40 mg L^{-1}. It is due to the SS reported.

It was found that the q_e obtained in the pseudo-first-order and pseudo-second-order models are closer to the experimentally obtained values. The fit of these two models to the data indicates that the process is controlled by chemisorption or ion exchange. This fact is due to the presence of the porous surface of the carbon-type materials. It also could be related to the appearance of multilayer adsorption and vertical packing of adsorbate in active centers [23]. The fit to the pseudo-first-order model represents the

Table 1
Kinetics and isotherm models [33]

Model	Equation	Parameters
Adsorption kinetics models		
Pseudo-first-order	$q_t = q_e\left(1-e^{-k_1 t}\right)$	q_e (mmol g^{-1}) is the adsorption capacity at equilibrium; q_t is the adsorption capacity at t time; k_1 (min^{-1}) is the constant of the velocity of reaction pseudo-first-order.
Pseudo-second-order	$q_t = \dfrac{t}{\dfrac{1}{k_2 q_e^2}+\dfrac{t}{q_e}}$	q_e (mmol g^{-1}) is the adsorption capacity at equilibrium; q_t is the adsorption capacity at t time; k_2 (g^{-1} min^{-1}) is the constant of the velocity of reaction pseudo-second-order.
Elovich	$q_t = \dfrac{1}{\beta}\ln(\alpha\beta)+\dfrac{1}{\beta}\ln(t)$	α (mg g^{-1} min^{-1}) is the Elovich initial adsorption velocity; β (g mg^{-1}) is the Elovich constant.
Intraparticle diffusion	$q_t = k_3^{1/2}$	q_t (mg g^{-1}) is the amount of metal adsorbed per unit mass of adsorbent in a time t (min); k_3 (mg g^{-1} min$^{-1/2}$) is the intraparticle diffusion constant.
Adsorption isotherm models		
Langmuir	$q_e = q_{\max}\dfrac{bC_e}{1+bC_e}$	q_e (mg g^{-1}) is the adsorbed metal concentration on the adsorbent; C_e (mg L^{-1}) is the residual metal concentration in solution; $q_{\max}$ (mg g^{-1}) is the maximum adsorption which corresponds to saturation sites.
Freundlich	$q_e = K_F C_e^{1/n}$	K_F (L mg^{-1} g^{-2}) is the Freundlich constant; n is the adsorption intensity; q_e (mg g^{-1}) is the adsorbed metal quantity.
Dubinin–Radushkevich	$q_t = q_{\mathrm{D-R}}e^{-k_{\mathrm{DR}}\varepsilon^2}$ $\varepsilon = RT\cdot\ln\left(1+\dfrac{1}{C_e}\right)$ $E = \dfrac{1}{\sqrt{2K_{\mathrm{DR}}}}$	ε^2 is the potential of Polanyi; K_{DR} is the Dubinin–Radushkevich constant related to adsorption energy (mol^2 kJ^{-2}); E is the average adsorption energy per adsorbate molecule required to transfer one mole of the ion from the solution to the adsorbent surface (kJ mol^{-1}); R is the gas constant (8.31 J mol^{-1} K^{-1}); T is the absolute temperature.

binding of the contaminant to an adsorption site on the surface of the biofuels, the rate being proportional to the number of unoccupied adsorption sites. [24]. The q_e calculated by the pseudo-first-order model is closer to the experimental q_e. Therefore, it is valid to say that this model better adjusts the adsorption of ibuprofen when using the CA 1:3 in all the concentrations evaluated and the CA 1:2 at 20 and 30 mg L^{-1}.

From the fit of the adsorption process of ibuprofen at 40 mg L^{-1} using carbon 1:2, it could be assumed that the removal of the contaminant takes place inside the pores of the adsorbent material due to its heterogeneity due to the better fit of the Elovich model. Therefore, the process is being controlled by chemisorption and occurs in multilayers [25]. It is observed that the Elovich parameter, α, decreases as the initial concentration of contaminant increases, indicating that the adsorption of ibuprofen diminishes. Likewise, $1/\beta$ indicates that at 40 mg L^{-1} the adsorbent has 1.3 available sites for adsorption [26].

The initial concentration of pollutants is an important parameter when studying adsorption processes since the amount of sorbate favors the mass transfer from the liquid to the surface of the material [27]. Fig. 2 showed the adsorption kinetics of ibuprofen and the adjustment to the pseudo-first-order, pseudo-second-order and Elovich models, at different initial concentrations of ibuprofen in the solution using the synthesized carbon with a 1:3 impregnation ratio (CA 1:3).

From the graphs shown in Fig. 2, rapid adsorption is observed in the first minutes of the process, which is attributed to the presence of an extensive network of transport pores in the synthesized activated carbon and used in the present study [28]. From Table 3, it can be established that using the CA 1:3 the pseudo-second-order model is the one that adjusts better the adsorption data at 20 and 30 mg L^{-1}. Additionally, the obtained q_e approaches to the experimental one, which coincides with the results obtained in different studies using ordered mesoporous carbons [29], *Artemisia* [30], mung beans [15], *Parthenium hysterophorus* [27]. The fit of the experimental data to the pseudo-second-order model indicates the adsorption of the pollutant by two active sites at the same time. Moreover, chemisorption might be the limiting step of the adsorption process speed where electrons share or exchange valence

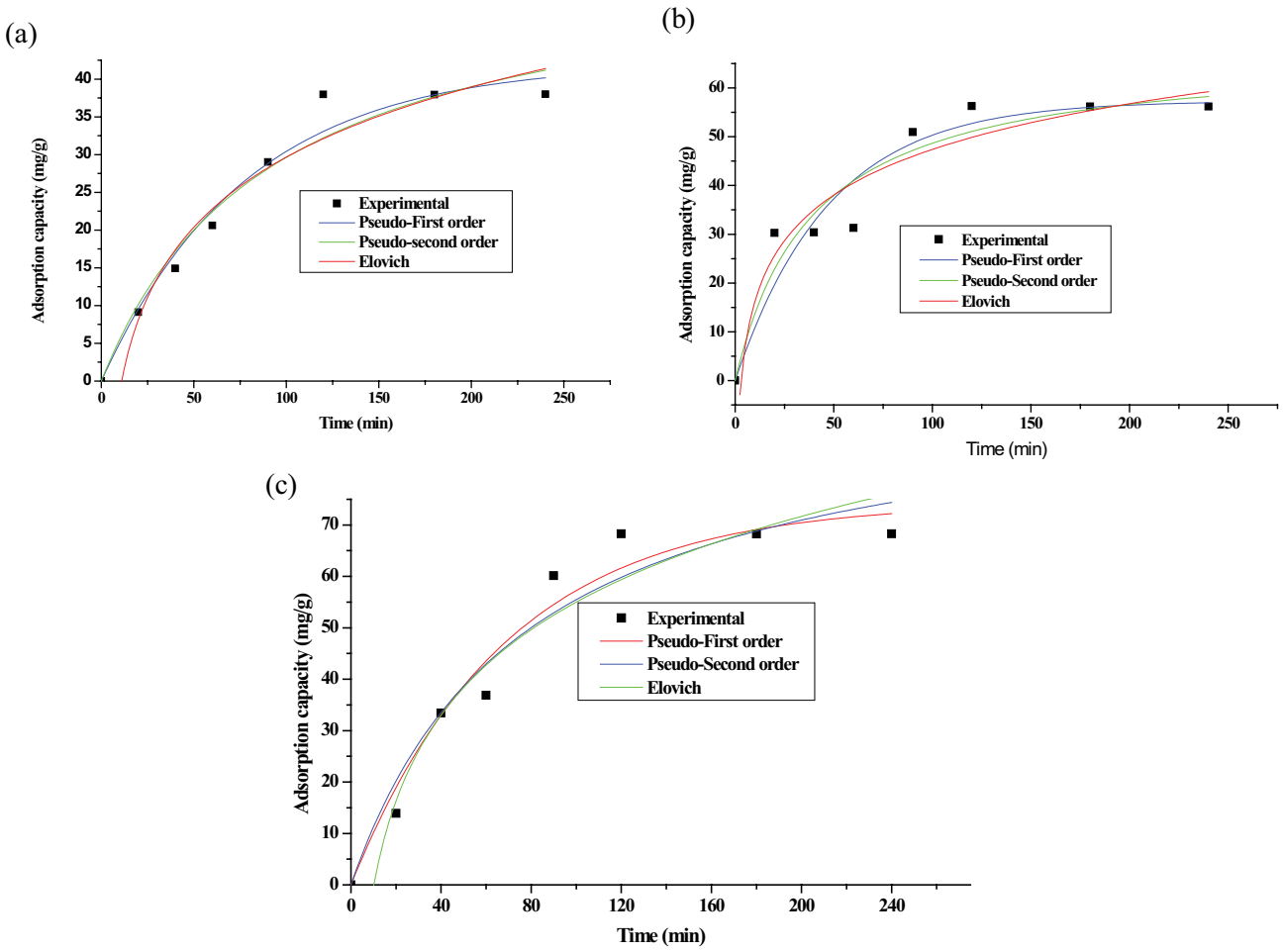

Fig. 1. The fit of the experimental adsorption data of ibuprofen at (a) 20 mg L^{-1}, (b) 30 mg L^{-1}, and (c) 40 mg L^{-1} on CA 1:2.

Table 2
Fitted parameters of the kinetic models of ibuprofen adsorption for CA 1:2

Kinetic model	Parameters	Value at different concentrations of ibuprofen		
		20 mg L^{-1}	30 mg L^{-1}	40 mg L^{-1}
Pseudo-first-order	q_{e1} (mg g^{-1})	42.113	57.339	74.405
	k_1 (min^{-1})	0.013	0.021	0.015
	SS	0.188	5.873	2.300
	R^2	0.951	0.902	0.963
Pseudo-second-order	k_2 (g mg^{-1} min^{-1})	0.217	0.021	0.013
	q_{e2} (mg g^{-1})	57.056	67.802	98.368
	SS	0.224	3.749	5.448
	R^2	0.958	0.954	0.945
Elovich	β (mg g^{-1})	1.226	4.508	0.041
	α (mg g^{-1} min^{-1})	0.0746	0.074	5.599
	SS	0.339	18.857	9.196
	R^2	0.934	0.914	0.824
Intraparticle diffusion	k_3	22.986	41.796	52.866
	R^2	0.343	0.577	0.484
	SS	3.356	3.768	5.749

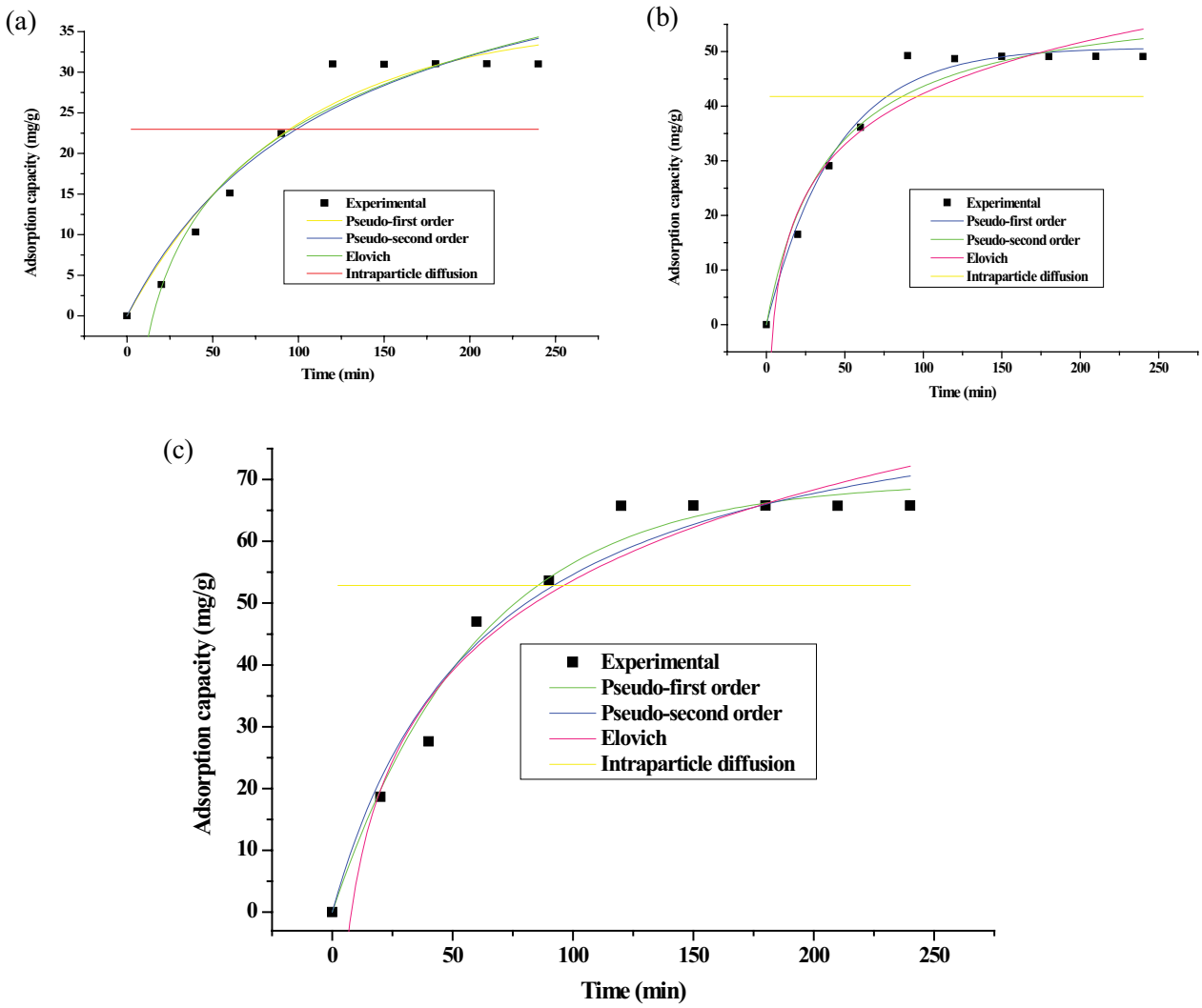

Fig. 2. The fit of experimental adsorption data from ibuprofen absorption at (a) 20 mg L^{-1}, (b) 30 mg L^{-1}, and (c) 40 mg L^{-1} using CA 1:3.

Table 3
Fitted parameters of the kinetic models of ibuprofen adsorption for CA 1:3

Kinetic model	Parameters	Values at different concentrations of IBP		
		20 mg L^{-1}	30 mg L^{-1}	40 mg L^{-1}
Pseudo-first-order	q_{e1} (mg g^{-1})	36.166	50.746	69.692
	k_1 (min^{-1})	0.011	0.023	0.017
	SS	0.428	0.367	0.159
	R^2	0.955	0.984	0.984
Pseudo-second-order	k_2 (g mg^{-1} min^{-1})	1.552	4.094E-4	1.779E-4
	q_{e2} (mg g^{-1})	51.871	61.088	89.107
	SS	0.129	0.126	0.271
	R^2	0.943	0.962	0.964
Elovich	β (mg g^{-1})	0.821	3.112	2.682
	α (mg g^{-1} min^{-1})	0.081	0.074	0.956
	SS	0.133	0.027	1.397
	R^2	0.955	0.941	0.956

forces between sorbate and adsorbent [31]. When evaluating the fit of the intraparticle diffusion model, it was found that it does not describe the experimental data, so it can be said that the adsorption process would be dominated by mass transfer and ion exchange between the surface of the adsorbent and the contaminant [31].

3.2. Adsorption equilibrium

The study of adsorption isotherms helps establish the distribution of the contaminant in the liquid and solid phase in the equilibrium. The fitted parameters of the different isothermal models were obtained at equilibrium time. The fit of the experimental data corresponding to the adsorption equilibrium employing coals at impregnation ratios of 1:2 and 1:3 is shown in Fig. 3. The parameters of the isothermal models were evaluated by non-linear regression and were shown in Table 4.

Considering the low values of the statistical error (Table 4) and the graphic adjustment shown in Fig. 3, the Freundlich model is the one that describes best the adsorption process. Therefore, it is assumed that the formation of multilayers on the surface of the biomass is carried out with an uneven distribution of heat and adsorption affinities on the heterogeneous surface during the process. The adsorbed molecules can interact with each other because of their distribution and close distance between the active binding sites [32].

The value of the Freundlich constant n using the two adsorbents is in a range of 1 to 10 using the CA 1:2 ratio. Which explains more favorable adsorption for mercury than for chromium. Also, since the n value is in the range of 1 to 10, it indicates that the adsorption process is favorable using both coals [33]. Besides, it is observed in Fig. 3 and according to the reported SS in Table 3, that the Langmuir model also acceptably fits the adsorption equilibrium data using CA 1:2, reaching a maximum adsorption capacity of 123.694 mg g^{-1}. However, the Langmuir equilibrium coefficient (b) reported low values. Therefore, low adsorption capacity is expected in the present study. Accordingly, the adsorption mechanism on the tested bio adsorbents is expected to be controlled by van der Waals forces [34].

From the fit to the Dubinin–Radushkevich model, it is established that it describes the adsorption balance on CA 1:2, with an average energy of adsorption of ions by sorbate (E) of 436.104 kJ mol^{-1}, which is much higher than 8 kJ mol^{-1}, indicating that the process is mostly controlled by chemical adsorption with strong interactions between active sites and Cr(VI) [34]. Similarly, the calculated maximum adsorption capacity (q_{DR}) values are the closest to the experimental ones with $R^2 \geq 0.9$.

4. Conclusions

It was found that by using initial contaminant concentrations of 20 and 30 mg L^{-1} using CA 1:2 and CA 1:3, the system behavior is more stable over the time when the pseudo-first and pseudo-second-order models adjust the experimental data. Likewise, when the initial concentration of pollutant is 40 mg L^{-1}, the experimental data is adjusted

Table 4
Fitted parameters from isotherm models

Isotherm model	Parameters	Value	
		CA 1:2	CA 1:3
Langmuir	q_{max} (mg g^{-1})	123.694	75.399
	b (1 mg^{-1})	0.101	6.147
	SS	0.1667	5.027
	R^2	0.929	0.926
Freundlich	K_F (mg L^{-1} g^{-2})	17.2	2.55
	n	0.552	1.243
	n	1.81	0.813
	SS	0.277	0.018
	R^2	0.882	0.994
Dubinin–Radushkevich	q_{DR}	76.456	93.503
	K_{DR}	2.629E-6	9.974E-6
	E	436.104	223.898
	R^2	0.999	0.9792
	SS	0.126	6.499

SS is the sum of squares.

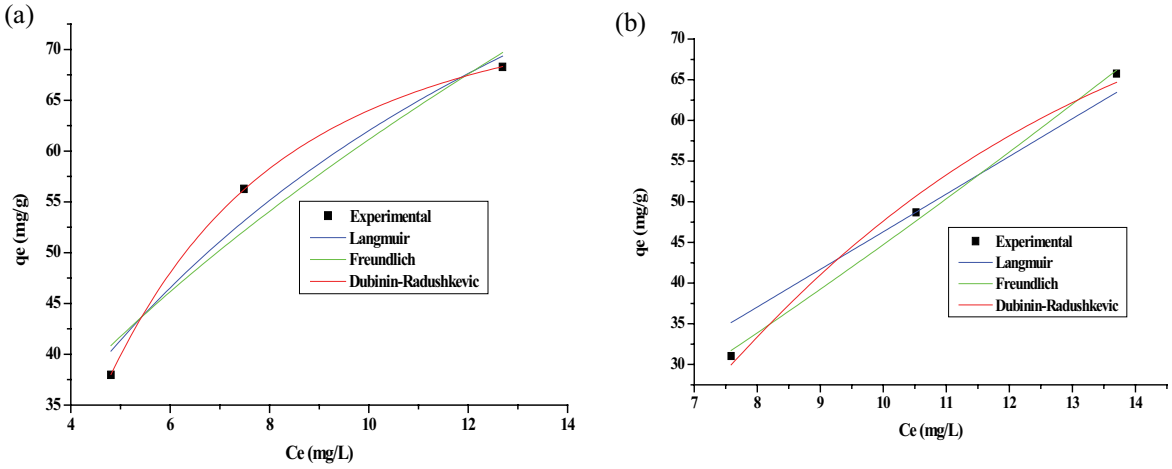

Fig. 3. The fit to the Langmuir and Freundlich isotherm models for the (a) CA 1:2 and (b) CA 1:3 coals.

by the Elovich model, being a chemisorption ruled process. Adsorption isotherms indicate that the Dubinin–Radushkevich model adjusted the equilibrium on CA 1:2 and that of Freundlich on CA 1:3. From which was established that the adsorption process is controlled by a chemical reaction in the different porous layers of the adsorbent. According to the Langmuir isotherm, a maximum adsorption capacity of 123.694 mg g^{-1} was achieved using CA 1:2, presenting this impregnation ratio as recommended to prepare activated carbon from cocoa husks for application in the ibuprofen removal. However, temperatures of 150°C–350°C are considered not to be sufficient for efficient carbonization due to the surface area obtained compared to other types of activated carbon. A novel porous biomaterial is proposed to be prepared at a low temperature and with a large surface area. This fact makes it low cost and promising from low energy consumption and opens a path for future research to test the removal of other drugs on a laboratory scale and transferring technology to the implementation of water treatment contaminated.

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Symbols

C_e	—	Residual metal concentration in solution, mg L^{-1}
E	—	Average adsorption energy per adsorbate molecule required to transfer one mole of the ion from the solution to the adsorbent surface, kJ mol^{-1}
k_1	—	Constant of the velocity of pseudo-first-order reaction, min^{-1}
k_2	—	Constant of the velocity of reaction pseudo-second-order, g^{-1} min^{-1}
k_3	—	Intraparticle diffusion constant, mg g^{-1} $min^{-1/2}$
K_{DR}	—	Dubinin–Radushkevich constant related to adsorption energy, mol^2 kJ^{-2}
K_f	—	Freundlich constant, mg L g^{-2}
n	—	Adsorption intensity
q_e	—	Adsorpted metal concentration on the adsorbent, mg g^{-1}
q_e	—	Adsorpted metal quantity, mg g^{-1}
q_e	—	Adsorption capacity at equilibrium, mmol g^{-1}
q_{max}	—	Maximum adsorption which corresponds to saturation sites, mg g^{-1}
q_t	—	Adsorption capacity at a t time
R	—	Gas constant 8.31 J mol^{-1} K^{-1}
T	—	Absolute temperature, K
α	—	Elovich initial adsorption velocity, mg g^{-1} min^{-1}
β	—	Elovich constant, g mg^{-1}

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