

Utilization of *Moringa oleifera* seeds as a biosorbent for diclofenac removal in the contaminated aquatic systems

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ABSTRACT

During recent years, pharmaceuticals and their metabolites have been increasingly found in water bodies and diclofenac is one of the pharmaceuticals residues most frequently detected thus far. The aim of this work was to evaluate the *Moringa oleifera* seeds as an alternative for diclofenac (DCF) removal in water samples. The batch procedure for DCF removal at the optimized conditions (25 mL of 10.0 mg L⁻¹ DCF, pH 5.0, extraction time of 30 min and *M. oleifera* mass of 2.0 grams) achieved adsorption of 100% of DCF in real water samples. The pseudo-second-order kinetic described the adsorption rate-controlling step. The adsorption isotherms were fitted by Langmuir, Freundlich and Sips models and the sorption capacity of the biosorbent is spontaneously favourable. The maximum adsorptive capacity was estimated at 32.05 mg g⁻¹ and 32.85 mg g⁻¹ by Langmuir and Sips models, respectively. The advantages of this procedure include good reproducibility in the removal of DCF even at low concentrations in real samples and does not require an additional step of pre-treatment of the adsorbent. The results highlight the potential of *M. oleifera* seeds as a cheap, environmentally friendly alternative for the removal of DCF from polluted water.

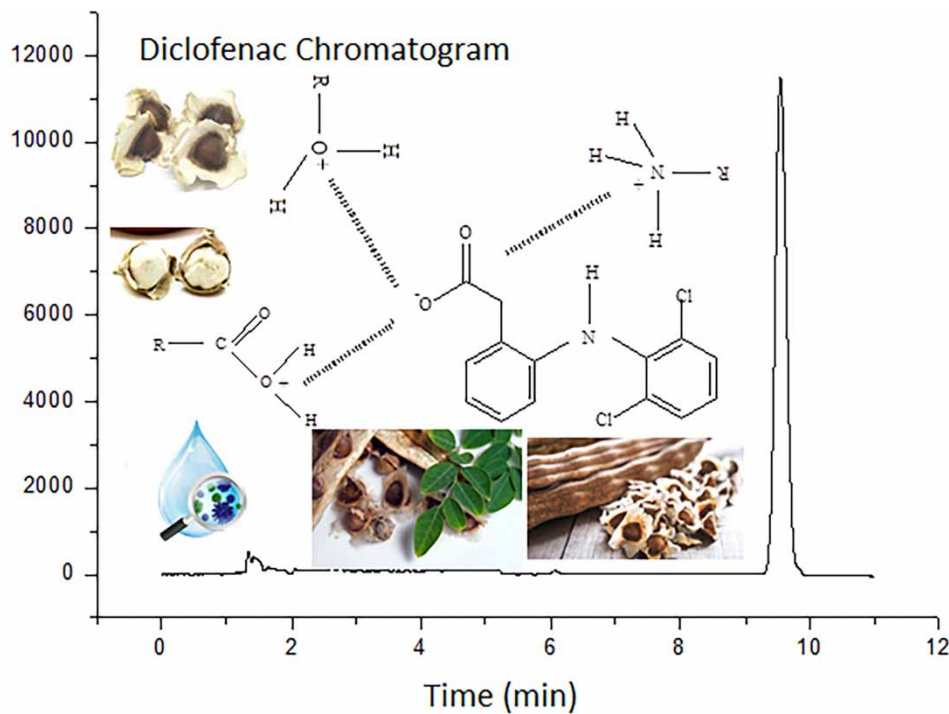
Key words: biosorbent, diclofenac, emerging contaminants, moringa oleifera, remediation, water

HIGHLIGHTS

- *Moringa oleifera* seeds were efficient in the adsorption of diclofenac obtaining removals greater than 95%.
- The adsorptive capacity of moringa was sufficient for remediation of contaminated water without any structural change of the adsorbent.
- The adsorption rate is determined by the chemical interactions.
- Adsorption equilibrium is reached spontaneously.
- The procedure was satisfactorily applied to real environmental samples.

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GRAPHICAL ABSTRACT



INTRODUCTION

The presence of emerging contaminants in the aquatic environment has been subject of increasing concern due to their effects on the environment and on the human health even at low concentrations ($\leq \mu\text{g L}^{-1}$). In this category, pharmaceuticals are the contaminants most frequently detected due to its widespread use (Izadi *et al.* 2020). Diclofenac (DCF) is a nonsteroidal anti-inflammatory drug that is widely prescribed in human and veterinary medicine with analgesic and anti-pyretic properties (Naghipour *et al.* 2018; Xu *et al.* 2020). Although the DCF's ecotoxicity is relatively low, if it interacts with other drugs present in water, the toxicological potential increases considerably (Xu *et al.* 2020). Surface and ground water contaminated by DCF can cause extensive damage to biota, e.g., feminization of fish (Medina *et al.* 2021); therefore, this compound has been recently included in the List of Priority Contaminants, regulated by 2013/39/EU Directive (Medina *et al.* 2021).

Previous studies demonstrated that DCF is not removed or is partially eliminated in conventional water treatment plants (Xu *et al.* 2020; Medina *et al.* 2021). Therefore, it is necessary innovative and alternative technologies to removal DCF and other drugs in contaminated water. Advanced oxidation process (AOP) is innovative alternative to removal organic contaminants in water (Alkhouraji 2019). However, the efficiency of these processes is considerably improved by the addition of chemical species, and additional techniques such as ultrasound radiation (Zhuan & Wang 2020). In addition, such procedures should be aware to the formation of degradation by-products with unknown toxicity. Also, considerable attention has been given to use of activated carbon (AC) for the adsorption of pharmaceuticals from aqueous solutions (Naghipour *et al.* 2018). Despite the efficiency of these procedures, they involve the use of chemical reagents, which may make them economically unfeasible. A promising alternative for the treatment of effluents that contain pharmaceuticals are natural adsorbents as a substitute for AC. Studies involving the use of biomass for the adsorption of pharmaceuticals are still scarce in the literature.

Moringa oleifera is a fast-growing tree that can reach 12 meters high found mainly in semiarid, tropical, and subtropical areas. Several applications have been proposed for *M. oleifera*, as its use in malnutrition and animal feed (Gopalakrishnan *et al.* 2016). The seeds have been used for the treatment of turbid water due to their flocculation properties (Baptista *et al.* 2017) and applied to textile effluent treatment (Agarwal *et al.* 2019). Other studies describe their use for the treatment of aqueous solutions containing silver (Araújo *et al.* 2010a), nickel (Marques *et al.* 2012) and chromium (Matouq *et al.* 2021) ions. However, there are still few reports available on the use of *M. oleifera* seeds, in their entirety, without the need for any structural change, for the adsorption of pharmaceuticals as DCF.

In this study, *M. oleifera* seeds were evaluated as a new low-cost adsorbent to remove DCF from the public potable water supply, river water and groundwater. The parameters that affect DCF adsorption (adsorbent dosage, pH, extraction time) were evaluated. Several models were carried out to determine the most suitable kinetic model and isotherm to explain the results. The use of *M. oleifera* seeds has certain advantages from both economic and environmental points of view, such as availability, the renewable nature of the adsorbent material, easy operation and their low cost.

METHODS

Instrumentation

Determination of diclofenac was performed using high-performance liquid chromatography – HPLC (Shimadzu, Kyoto, Japan) equipped with C18 column (150 × 4.6 mm, 5 μm diameter) and UV/VIS SPD-10A detector set at 282 nm. Acetonitrile and 0.10% (v/v) acetic acid (1:1) mixture was used as mobile phase.

Reagents and solutions

All solutions were prepared using ultrapure water (18 MΩ cm), analytical grade reagents and HPLC grade solvents. Diclofenac sodium (DCF) (molecular weight = 318.1 g mol⁻¹; chemical formula = C₁₄H₁₀C₁₂NNaO₂; pKa = 4.2) was purchased from Sigma Aldrich (Rome, Italy). Working solutions (0.5–100.0 mg L⁻¹) were prepared from the dilution of the 1,000 mg L⁻¹ DCF. Acetonitrile used as mobile phase was purchased from Sigma Aldrich. Prior to use, all glassware was kept overnight in 10% (v/v) aqueous nitric acid solution, followed by ultrasonication for 1 hour and finally washed with deionized water. Samples and solvents were filtrated in cellulose acetate membranes (Chrom filter) with 0.45 μm pores.

Preparation of adsorbent material

The *M. oleifera* seeds used as adsorbent material were collected in the city of Uberlândia-Brazil (latitude 18°55'07" S and longitude 48°16'38" W). After collecting the material, the pods were shelled and the seeds were washed twice with deionized water and left in an ultrasound bath for 10 minutes. Then, the seeds were dried in the open air (24–28 °C) for 8 hours in a dust-free environment. The dried seeds were ground in a commercial blender. Seed powders were separated according to particle size, using a sieve shaker with defined granulometry meshes. A particle size range of 0.5–1.0 mm was selected for further experiments. The material characterization was presented in previous works (Araújo *et al.* 2010b).

Batch adsorption procedure

DCF removal studies were performed by adding the prepared biosorbent in 10 mg L⁻¹ diclofenac solutions. The mixture was shaken for 30 min in a magnetic stirrer and then the suspension was filtered through filter paper (Whatman N°42). The filtrate was diluted with mobile phase before HPLC analysis. DCF was quantified before and after the removal experiments. In order to achieve the optimum conditions in terms of diclofenac removal, the following variables were evaluated: adsorbent mass (0.5 to 2.0 g) and stirring time (5 to 1,440 min). The pH was maintained at 5.0 during all experiments. DCF removal percentage was estimated by the following equation:

$$\% \text{Adsorption efficiency} = \frac{(C_o - C_f)}{C_o} \times 100 \quad (1)$$

where C_o and C_f (mg L⁻¹) are DCF concentration before and after the adsorption process, respectively.

Adsorption kinetic models and isotherms

The experiments to investigate the adsorption kinetics were carried out in the temperature range of 25–28 °C using 0.5 g of *M. oleifera* seeds powder, 25 mL of 10.0 mg L⁻¹ DCF solution at pH 5.0, and stirring time up to 30 min. These same conditions were applied to adsorption isotherm experiments, except that the concentration of DCF varied from 0.5 to 100.0 mg L⁻¹. In both experiments, these conditions were applied to ensure the achievement of the equilibrium state; mixtures were then filtered and DCF quantified by HPLC.

In both studies, the DCF concentration after the adsorption (C_f) was used to calculate the adsorption capacity of DCF at equilibrium (q_e) in milligrams per gram of adsorbent, through Equation (2):

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

where V is the volume of the DCF solution in liters and m is the mass of the adsorbent material in grams.

Application of the proposed method

The method was applied using the biosorbent for to evaluated adsorption of diclofenac from potable water (public supply), river water, and groundwater. The sample of potable water treated by a local sanitation company was collected from a tap in a research laboratory in the city of Uberlândia (Brazil), and river samples were collected from three different locations along the Uberabinha River, which runs through an urban zone in the city of Uberlândia. In these samples, diclofenac was not detected. Thus, to assess the performance of the adsorbent material in these systems, the samples were spiked with 10.0 mg L^{-1} DCF. The samples were filtered through filter paper and the pH was adjusted to 5.0 using 0.1 mol L^{-1} HCl. The samples (25 mL) were then treated with 0.5 g of adsorbent and using a stirring time of 5 min. The DCF was quantified using HPLC before and after the removal experiments.

RESULTS AND DISCUSSION

Optimization of adsorption process

The adsorption efficiency of the biosorbent depends on parameters as pH, material amount and contact time. The initial concentration of DCF (10 mg L^{-1}) was selected in such a way that the lowest concentration expected after adsorption was within the limit of quantification of the equipment (0.37 mg L^{-1}). Regarding the particle size, the selected size range (0.5–1.0 mm) was for presenting the largest contact surface without the occurrence of agglomerations in the solution.

The pH of DCF solutions was set at 5.0 for all experiments based on characterization studies of the *M. oleifera* seeds presented by Araújo and collaborators (Araújo *et al.* 2010b). Its pH value of the point of zero charge is in the range of 6 to 7. Thus, below this pH range, the surface of the sorbent is positively charged and it is able to adsorb diclofenac as its anionic form that is predominant close to pH 5.0.

The effect of contact time on removal percentage of DCF sodium is shown in Figure 1. The adsorbed amount of DCF onto *M. oleifera* seeds increases with the increase of contact time and the equilibrium state is reached in about 120 min. Adsorption capacity presented a rapid increase during the first 60 min. This high adsorption capacity at the initial stage indicated higher driving force that made fast transfer of diclofenac to the surface of adsorbent particles. From Figure 1 the DCF removal efficiency was ca. 90%.

The effect of biosorbent mass on DCF removal was evaluated in the range of 0.5–2.0 g using an adsorption time of 30 min. The results are summarized in Figure 2. Removal efficiency increased up to 2.0 g of *M. oleifera* seeds. It is observed that the availability of adsorption sites is higher by employing more biosorbent mass, until a saturation trend is observed, which results in higher DCF removal.

Adsorption kinetics study

The study of adsorption kinetics provides important information regarding its mechanism and the limiting step that controls the adsorption rate (Ho & McKay 1999). The models used to assess the kinetics of the adsorption process that best fit the data are the pseudo-first-order models of Lagergren, the pseudo-second order of Ho & McKay (1999) and the intraparticle diffusion model (Weber & Morris 1963).

The equations that describe the kinetic models of pseudo-first order, pseudo-second order and intraparticle diffusion, respectively, are represented by Equations (3)–(5):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2,303} t \quad (3)$$

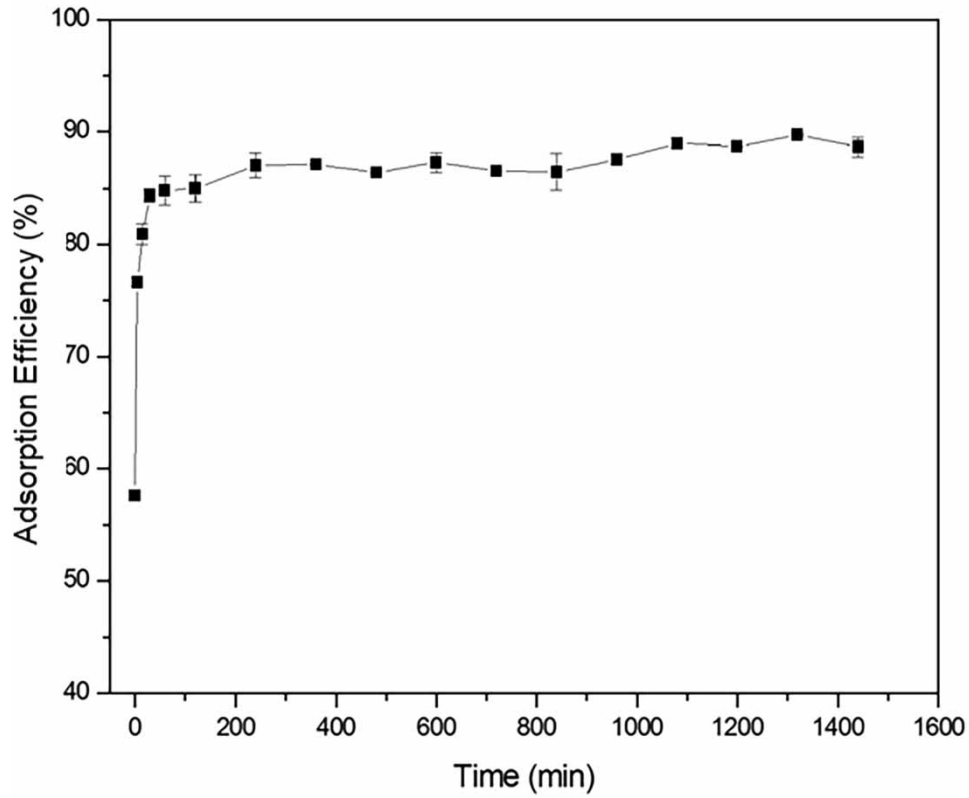


Figure 1 | Effect of the variation of the adsorption time. Conditions: Volume of the solution = 25.0 mL, pH = 5.0, Diclofenac concentration = 10.0 mg L⁻¹, Mass = 2.0 g of the adsorbent.

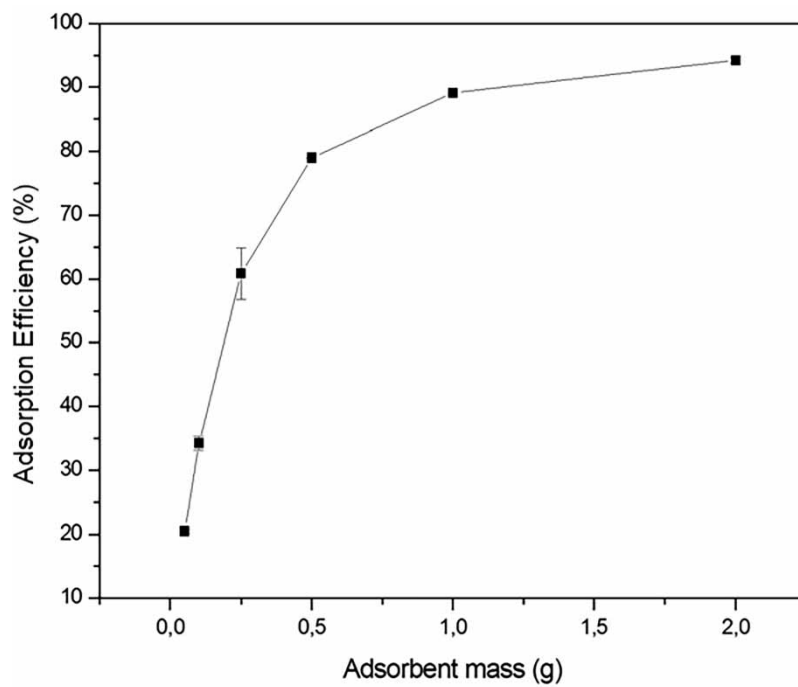


Figure 2 | Effect of varying the mass of the adsorbent. Conditions: Volume of the solution = 25.0 mL, pH = 5.0, DCF concentration = 10.0 mg L⁻¹, stirring time = 30 minutes.

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (4)$$

$$k_d = \frac{q_t}{t^{0.5}} \quad (5)$$

where q_e : adsorption capacity of DCF per gram of adsorbent at equilibrium (mg g^{-1}); q_t : adsorption capacity of DCF per gram of adsorbent at time t (mg g^{-1}); k_1 : pseudo-first-order velocity constant (min^{-1}); k_2 : pseudo-second order velocity constant ($\text{g mg}^{-1} \text{min}^{-1}$) and k_d : intraparticle diffusion coefficient ($\text{mg g}^{-1} \text{min}^{-0.5}$).

The parameter values obtained from the linear fit for the pseudo-first order and pseudo-second order models are summarized in Table 1.

Table 1 | Results of the kinetic parameters of the adsorption process of DCF by moringa seeds

Pseudo-first order				Pseudo-second order			
r^2	q_e (mg g^{-1})	k_1 (min^{-1})	χ^2	r^2	q_e (mg g^{-1})	k_2 ($\text{mg}^{-1} \text{g min}^{-1}$)	χ^2
0.9772	0.06994	0.1287	0.04176	0.999	0.0962	13.4386	0.0001086

$q_{e, \text{exp}} = 0.1060 \text{ mg g}^{-1}$.

The pseudo-first-order adsorption kinetics plot of the DCF on the moringa is shown in Figure 3(a). The coefficient of determination is relatively low. Furthermore, the experimental q_e value does not agree with the one calculated using this model, indicating that adsorption does not is controlled only by the number of active sites available in the adsorbent.

As can be seen in Table 1, the coefficient of determination for the pseudo-second-order kinetic model is the one that best fit, indicating that the adsorption process fits the pseudo-second-order mechanism. The pseudo-second-order adsorption kinetics plot of the drug DCF on the moringa is shown in Figure 3(b). This model assumes that the determining step of the adsorption rate depends on the physicochemical interactions between the adsorbent and the available groups on the surface of the adsorbent in its entirety. In addition, the adsorption process on the surface of the adsorbent is proportional to the number of sites occupied (Ho & McKay 1999; Ahmad *et al.* 2005).

The intra-particle diffusion model was also tested to obtain more information about the mechanism involving the formation of a permeable film, which can diffuse into the pores of the adsorbent (Weber & Morris 1963).

As can be seen in Figure 4, the data plotted in relation to intra-particle diffusion does not represent a satisfactory linear fit; therefore, it cannot be elucidated mathematically by a single equation. The curve obtained does not pass through the origin and the graph is not linear throughout the process, suggesting that the intraparticle diffusion mechanism is not dominant. Thus, the data are better represented by two linear phases. The initial phase representing the effect of the boundary layer, with external mass transfer. In this case, DCF is rapidly adsorbed by moringa seeds. After some time, the equilibrium is observed, resulting in the second phase. In this case, due to the low concentration of solute in the solution as well as a lower availability of sites for adsorption, the effect of intraparticle diffusion is decreased.

To evaluate the fit of the parameters obtained in the tested linear regression models for the pseudo-first-order and pseudo-second-order kinetics, the experimental q_e values were compared with the respective fitted values for each contact time until reaching the equilibrium (120 min). The comparison profile is shown in Figure 5, the raw results of which are shown in Table 1 of the supplementary data. The pseudo-second order model presents values of q_e that are closest to the experimental results. The obtaining a smaller magnitude of the error function (χ^2) in relation to the pseudo-first order confirms the adequacy of the performed fit.

The performance of moringa seeds as an alternative adsorbent has presented similar conditions for satisfactory removal of other drugs. In a similar work, pseudo-second-order kinetics was also shown to be adequate to describe the limiting step of paracetamol adsorption, as reported by Ogunmodede *et al.* (2021).

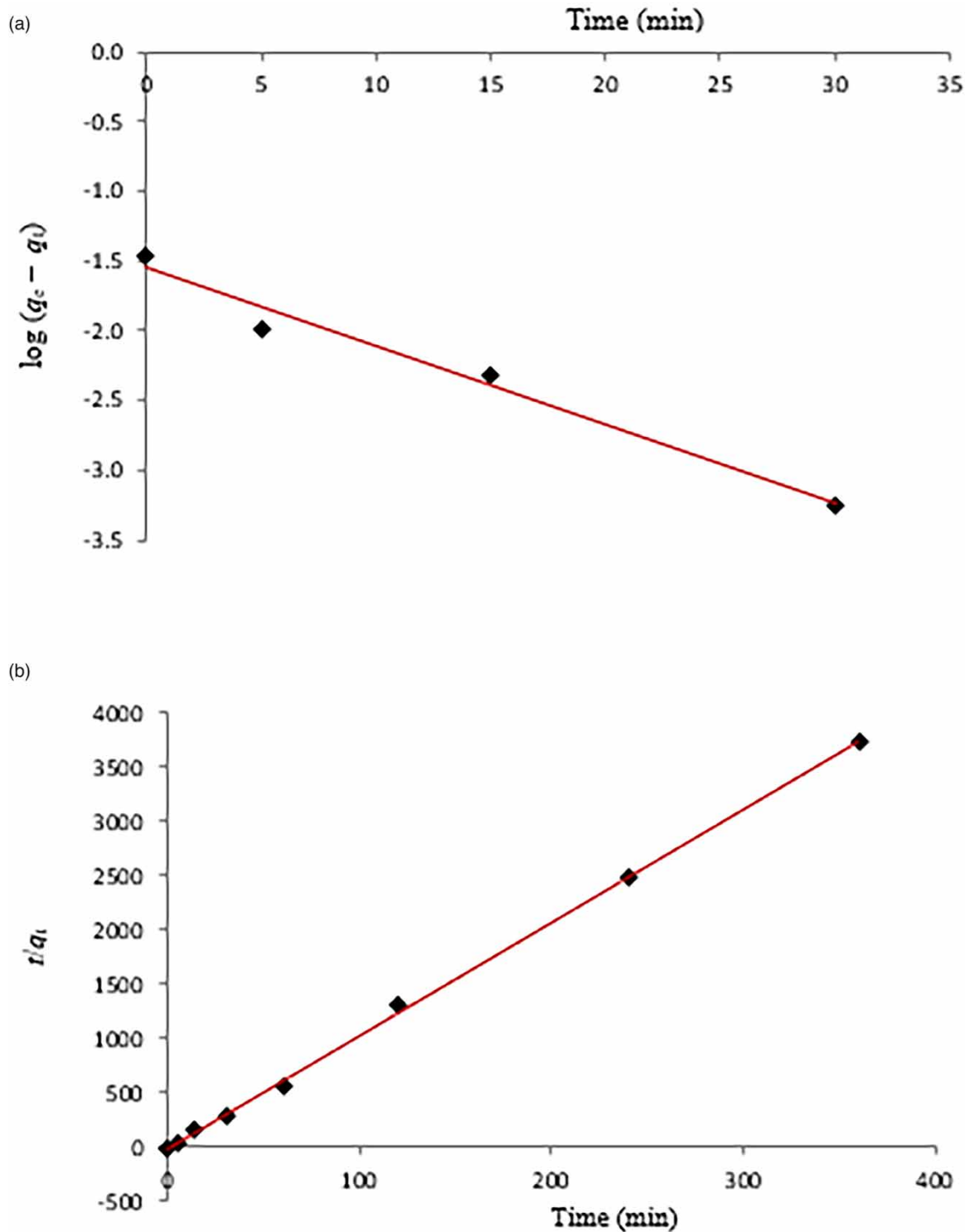


Figure 3 | Linear fit applied to (a) pseudo-first-order and (b) pseudo-second-order adsorption kinetic models.

Adsorption isotherms

Figure 6 shows the adsorption isotherm for DCF adsorption onto *M. oleifera* seeds. Among the isotherm models found in the literature, the primary ones are the Langmuir (Langmuir 1918) and Freundlich (Freundlich 1906).

The Langmuir model assumes that adsorption is limited to the monolayer; a maximum adsorption indicates the saturation of this monolayer. The fitting of the experimental data to the Langmuir linear equation can be

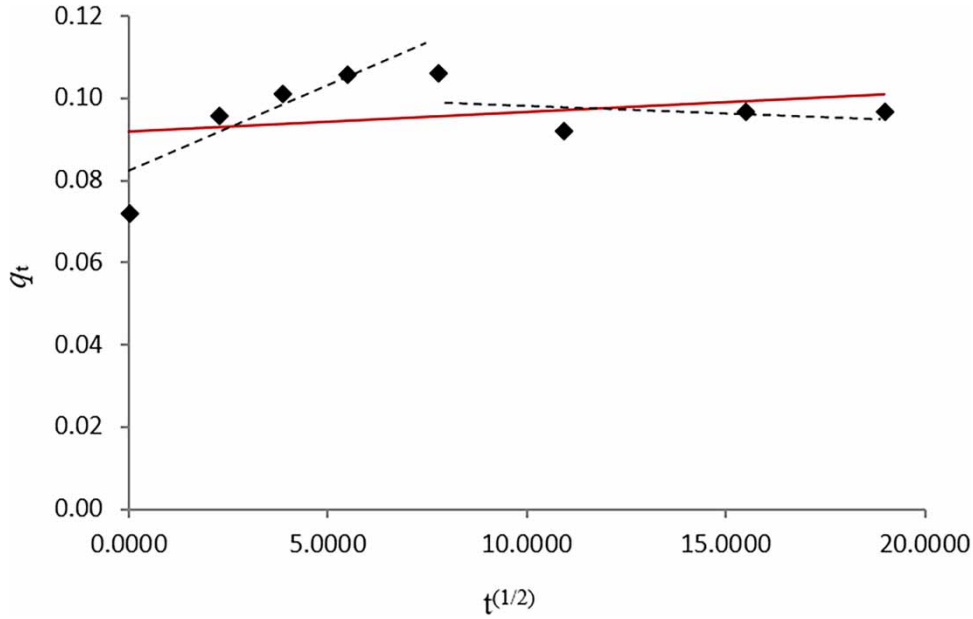


Figure 4 | Plot of data obtained from the application to the intra-particle diffusion kinetic model.

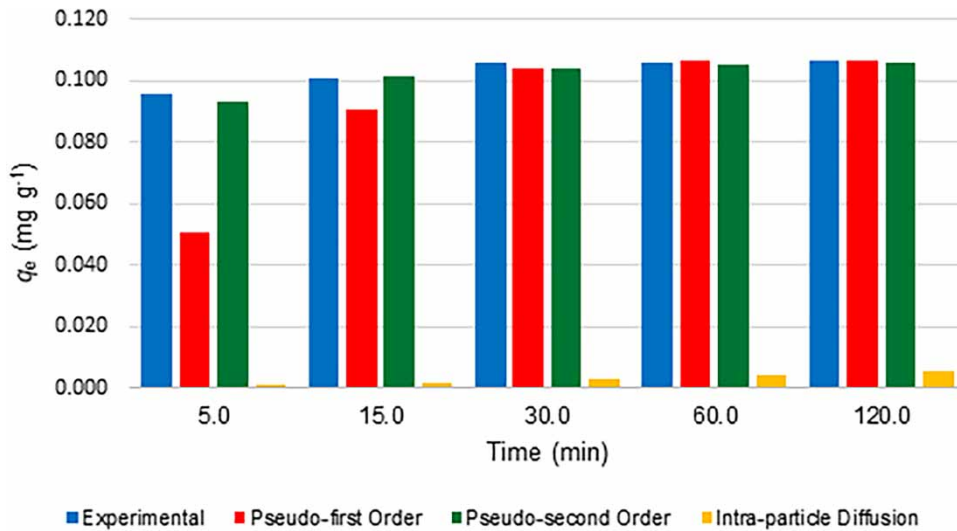


Figure 5 | Comparison profile between the experimental results and the kinetic models tested.

expressed by the following equation:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max}K_L C_e} \tag{6}$$

where C_e (mg L^{-1}) is the equilibrium concentration of the DCF, q_e (mg g^{-1}) is the adsorption capacity of DCF adsorbed per unit mass of the adsorbent at equilibrium, q_{max} (mg g^{-1}) is the maximum adsorptive capacity, and K_L (L mg^{-1}) is the Langmuir constant related to the adsorption capacity.

The value of K_L was used to calculate the R_L parameter according to Equation (7). This admission constant R_L is called the equilibrium parameter, being a measure of favoring adsorption. R_L values between 0 and 1 represent a favorable adsorption process explained by the Langmuir isotherm (Rao *et al.* 2006).

$$R_L = \frac{1}{(1 + K_L C_0)} \tag{7}$$

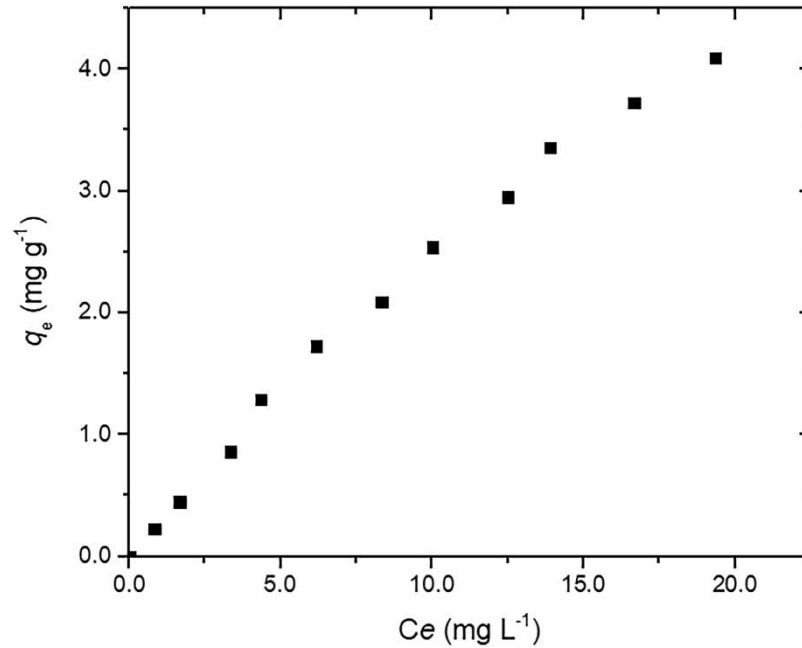


Figure 6 | Adsorption isotherm of DCF onto moringa seeds. Conditions: pH = 5.0; diclofenac concentration = 0.5 to 100.0 mg L⁻¹, Stirring time = 30 minutes and the adsorbent mass = 0.5 mg.

Figure 7(a) presents the data according to Equation (6). The correlation coefficient obtained was 0.9991 and q_{\max} was estimated at 32.05 mg g⁻¹, which is similar the experimental q_{\max} (31.71 mg g⁻¹) value, thus showing that the data fit the Langmuir model as observed in the Figure 4(a).

The Freundlich isotherm is an empirical expression that takes into account the heterogeneity of the surface and multilayer adsorption onto the binding sites located on the surface of the sorbent. The Freundlich model is expressed as follows:

$$\log q_e = (1/n) \log C_e + \log K_F \quad (8)$$

where C_e (mg L⁻¹) is the equilibrium concentration of the metal, q_e (mg g⁻¹) is the adsorption capacity of DCF adsorbed per unit mass of the adsorbent at equilibrium, and n and K_F (mg g⁻¹) are the Freundlich constants related to the biosorption intensity and adsorption equilibrium constant, respectively.

Figure 7(b) was plotted according to Equation (8) and the values of n , and K_F are 1.0785 and 0.2894 respectively. The determination coefficient (r^2) obtained was 0.9943, thus showing that the experimental data provide a good fitted with the Freundlich model, as observed in Figure 4(b). The value of n was greater than 1, suggesting relatively strong adsorption of DCF onto the surface of moringa seeds.

The isotherm evaluation showed that the experimental data for adsorption of DCF onto moringa seeds provided a good fit to the two isotherm models. Despite that linear correlation (r^2) value of the Langmuir model is slightly higher than that of the Freundlich model (Table 2), it is reasonable to assume that DCF adsorption behavior onto biosorbent may take place in monolayer on the surface of the adsorbent. However, based on satisfactory correlation coefficients, the data are also consistent with a model in which the multilayers adsorption takes place on the adsorbent materials. This result is somewhat expected, bearing in mind the complexity of the structure and composition of the biosorbent.

With the interest in elucidating more clearly if there is a predominant adsorption mechanism, a new isotherm model Langmuir-Freundlich (or Sips isotherm) was tested. This isotherm can be representative of the characteristics predicted by the Langmuir or Freundlich isotherm in materials of heterogeneous composition, such as the moringa seeds. In this way, the Sips isotherm combines both isotherms in the same mathematical relationship, as

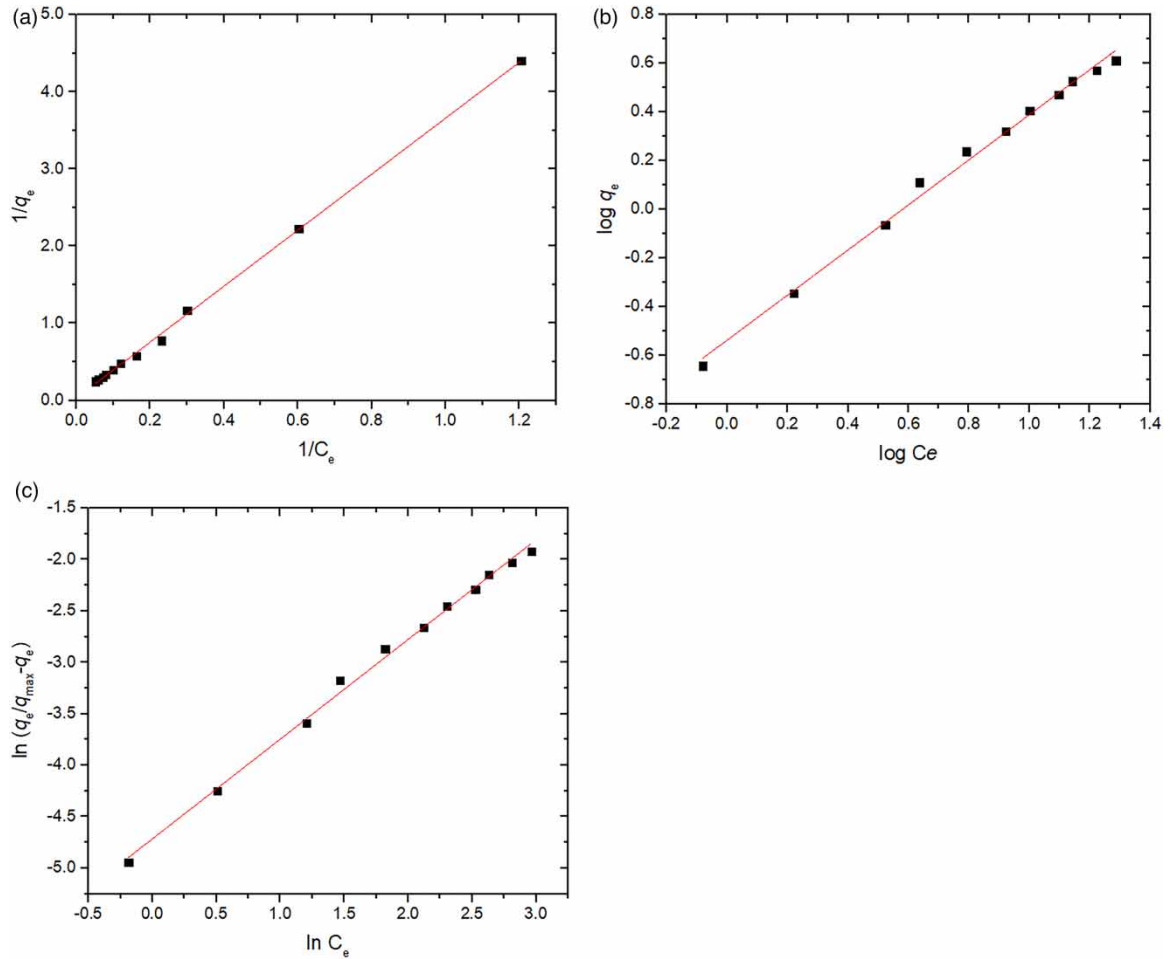


Figure 7 | Langmuir (a), Freundlich (b) and Sips (c) isotherm plots for the sorption of diclofenac onto *Moringa oleifera* seeds.

Table 2 | Equilibrium parameters of DCF adsorption onto *M. oleifera* seeds

Langmuir

q_{max} (mg g ⁻¹)	R_L	K_L (L mg ⁻¹)	K_L (L mol ⁻¹)	r^2	χ^2
32.05	0.0086	1.1528	366 702.72	0.9991	0.1074

Freundlich

K_F (mg g ⁻¹)(L g ⁻¹) ^{1/n}	n	r^2	χ^2
0.2894	1.0785	0.9943	0.0977

Sips

q_{max} (mg g ⁻¹)	K_s (μg L ⁻¹) ^{-1/n}	n	r^2	χ^2
32.85	0.00772	1.03156	0.9961	0.4433

shown by Equation (9) (Foo & Hameed 2010):

$$\ln\left(\frac{q_e}{q_{max} - q_e}\right) = \frac{1}{n} \ln C_e + \frac{1}{n} \ln K_s \tag{9}$$

For low initial concentrations of adsorbate this model assumes the Freundlich form, while at high concentrations, the Equation (9) assumes a form similar to the Langmuir isotherm, in monolayers. In the Sips

isotherm model, the constant K_s is associated with the adsorption energy and the parameter n which also represents the degree of heterogeneity. If $n = 1$ the system is homogeneous, equating to the Langmuir model, and for values of n increasingly smaller than 1, an increase in heterogeneity has been characterized. In the case of $n > 1$, it is indicative of the formation of more than one layer of adsorbate on the adsorbent (Foo & Hameed 2010). The results were plotted in the Figure 7(c).

The results present a satisfactory fit for the Sips isotherm, through the good value of the coefficient of determination 0.9961. The value of q_e predicted by the Sips (32.85 mg g^{-1}) model is appreciably close to that determined by the Langmuir isotherm. However, the highest value of the error function obtained in relation to the respective values for the Langmuir and Freundlich isotherms is notorious (Table 2). The Figure 8 illustrates the comparison profile between the experimental q_e values for each C_e , in relation to the tested isotherm models, the raw results of which are shown in Table 2 of the supplementary data.

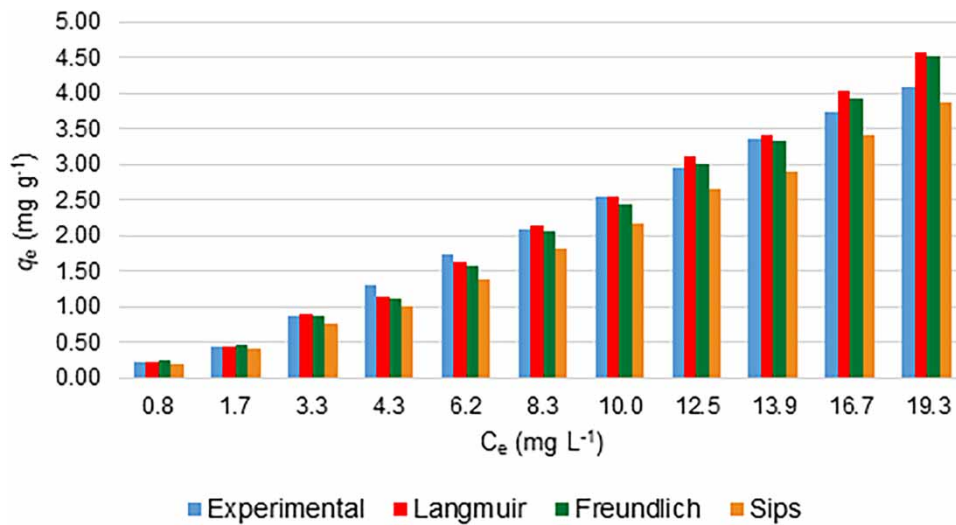


Figure 8 | Comparison profile between the experimental results and the tested adsorption isotherm models.

The good agreement of the experimental data with the Langmuir model suggests that the mechanism of adsorption of DCF onto moringa seeds occurs in a way defined by specific interactions at individual active sites. The parameters calculated by the Langmuir model are reasonable to indicate the reach of the adsorption equilibrium by the saturation of the active sites. The influence of material heterogeneity is related to the variation of the spatial orientation of the organic adsorbate on the surface, which may cause π - π interactions between the DCF molecules (Viotti *et al.* 2019). This explains the value of parameter n obtained in the Sips isotherm, slightly greater than 1.0.

Organic molecules such as diclofenac are limited to diffusing inside micropores, due to the size of molecules being relatively larger than micropores. As solid surfaces are rarely homogeneous, in addition to chemical reactions between the adsorbent and the adsorbate, the effects of the transport phenomenon in the inner portion of the adsorbate must be considered (Ho & McKay 1999), which is consistent with the experimental results obtained in this work, taking into account that the Langmuir and Freundlich isotherms obtained very similar and satisfactory coefficient of determination values.

The constant K_L was used to calculate the change in the standard Gibbs free energy ($\Delta G_{\text{ads}}^\circ$) for the adsorption of DCF by moringa seeds using Equation (10):

$$\Delta G_{\text{ads}}^\circ = -RT \ln K_a \quad (10)$$

where, R is the ideal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the absolute temperature (298 K), and K_a is the thermodynamic equilibrium constant (dimensionless), which can be calculated from the Langmuir constant, K_L , as discussed by Liu 2009. Since the adsorbate is an organic specie with weak charge, under these adsorption conditions, K_L was used as an estimate of the value of K_a (Liu 2009). The value obtained of $\Delta G_{\text{ads}}^\circ$ for the adsorption

of DCF by moringa seeds was $-32.7 \text{ KJ mol}^{-1}$, where the negative value indicated that the adsorption process was spontaneous, which is consistent with favoring the adsorptive process predicted by the Langmuir model.

Application

The method was applied using the biosorbent for evaluated adsorption of DCF in potable water (public supply) and river water. In these samples DCF was not detected, and thus, they were spiked at a concentration of 10.0 mg L^{-1} . The samples were subsequently treated with the adsorbent material and the diclofenac removal efficiency was estimated as shown in Table 3. The results achieved indicate the potentiality of the *M. oleifera* seeds as an effective tool for DCF removal from water samples.

Table 3 | Determination of DCF in water samples and experimental recovery of DCF in water samples spiked with 10.0 mg L^{-1} DCF

Samples	DCF found (mg L^{-1})	DCF added (mg L^{-1})	DCF after removal (mg L^{-1})	Removal (%)
Groundwater	0.20 ± 0.01	–	–	101.02
	0.20 ± 0.01	10.00	1.72 ± 0.02	83.14
Tap water	0.28 ± 0.04	–	–	100.8
	0.28 ± 0.04	10.00	1.83 ± 0.05	82.20
River water	n.d.	–	–	–
	n.d.	10.00	1.70 ± 0.01	83.05
Lake water	n.d.	–	–	–
	n.d.	10.00	1.88 ± 0.01	81.20
Rain water	n.d.	–	–	–
	n.d.	10.00	1.86 ± 0.01	81.40
Wastewater	0.12 ± 0.01	–	–	100.31
	0.12 ± 0.01	10.00	1.62 ± 0.09	83.80

N.D.: not detectable. ($n = 3$).

DCF removal efficiencies were greater than 95% under the experimental employed conditions (25 mL of 10.0 mg L^{-1} DCF, pH of 5.0, contact time 30 min and 2.0 mg of *M. oleifera* seeds). The results showed satisfactory reproducibility to removal low concentrations of DCF in the samples tested.

The adsorption efficiency of moringa seeds as a natural biosorbent, without any structural modification, as reported here, is comparable to other more expensive adsorption procedures. In a study involving the adsorption of DCF in fixed bed columns, using AC as a synthetic material, a maximum adsorptive capacity of 36.25 mg g^{-1} (298 K) was observed (Franco *et al.* 2018). In a similar work, Viotti *et al.* (2019), achieved good adsorptive capacity (60.805 mg g^{-1}) using *M. oleifera* pods for DCF removal in distilled water. However, a pre-treatment step of the adsorbent with $\text{HCl } 0.1 \text{ mol L}^{-1}$ was necessary. Satisfactory results could only be obtained by heating the system to 328 K. The authors concluded that under such conditions, the adsorption of DCF it is not spontaneous (Viotti *et al.* 2019).

Compared to other previously presented materials for DCF removal as hybrid inorganic materials (Thanh-mingliana & Tiwari 2015) or amended iron micro particles (Ghauch *et al.* 2010), the biosorbent based on *M. oleifera* seeds has advantages in high availability, easy material preparation, good adsorption capacity, cheap cost and potential applicability to removal of other organic and inorganic contaminants.

CONCLUSIONS

The evaluation of *M. oleifera* seeds as a biosorbent for DCF removal from potable water supplies demonstrated the high potential of this material as a cheap and environmentally friendly alternative for pharmaceutical remediation in water. DCF removal efficiencies were greater than 95% from water samples under the optimum experimental conditions. The use of moringa seeds without any structural change in their natural composition represented an advantage of this procedure. The results indicated that the rate-determining step of adsorption is controlled by specific interactions of an electrostatic nature between the DCF and the surface of the adsorbent, through pseudo-second-order kinetics. The Langmuir model proved to be adequate for adjusting the adsorption

isotherm. The maximum adsorptive capacity was estimated at 32.05 mg g⁻¹, which is consistent with the theoretical value. The satisfactory maximum adsorption capacity obtained and negligible cost of biosorbent means that moringa seeds can be considered as a reliable natural material for the removal of DCF from aqueous effluents.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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