DICLOFENAC REMOVAL FROM WATER BY MORINGA OLEIFERA SHELL BIOSORPTION

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Abstract:

In this study, the adsorption behavior of diclofenac (DCF) was investigated using moringa oleifera (MO) as a biosorbent. The pH dependence, kinetic parameters, and surface-charge interactions were studied to understand the adsorption mechanism. The results demonstrate that MO exhibits a positive surface charge at low pH values (<6) and a negative charge at higher pH values (>6), indicating electrostatic interactions with negatively charged DCF. Kinetic study revealed a significant removal percentage of approximately 75% within 90 min, suggesting the potential of MO as an effective adsorbent. The pH dependence of DCF adsorption was evident, with the highest removal observed at pH 2 and the lowest at pH 8. This study highlights the potential of MO as a promising biosorbent for DCF removal and emphasizes the need for further investigations to optimize the adsorption process and explore its wider applications in pharmaceutical removal.

Keywords: biosorption, diclofenac, kinetic, Moringa oleifera.

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1. INTRODUCTION

The presence of pharmaceuticals in surface water, wastewater, and drinking water streams has steadily increased over time [1]. The accumulation of drug residues in the environment has become a worldwide concern because even at extremely low concentrations, prolonged exposure to these contaminants can lead to bacterial resistance against drugs, compromising their effectiveness and posing a significant threat to the field of medicine [2].

In this study, we focused on investigating the environmental presence and impact of a specific drug, namely, the nonsteroidal anti-inflammatory drug (NSAID) diclofenac (DCF), chemically known as 2-[(2,6-dichlorophenyl)amino]phenylacetate. Diclofenac is commonly used to alleviate pain, particularly in the treatment of rheumatoid arthritis, osteoarthritis, musculoskeletal injuries, and postoperative analgesia in both humans and animals [3].

Diclofenac (DCF), a widely used nonsteroidal anti-inflammatory drug (NSAID), holds a prominent position in the NSAID group because of its high global consumption rate. It has been estimated that approximately 940 tons per year of diclofenac is consumed worldwide, with Europe alone accounting for approximately 180 tons per year, and countries such as China, India, and Brazil surpassing 60 tons per year [4]. Establishing typical concentration values of DCF in the environment is challenging. However, published results from various studies have provided some insights into the concentrations found. For instance, municipal wastewater samples revealed a DCF concentration range of 0.44 to 7.1 µg L^{-1}, while hospital wastewater showed a maximum concentration of 6.88 µg L^{-1}. In South Korea, pharmaceutical factories have been found to have concentrations as high as 203 µg L^{-1} [5]. In Pakistani rivers, DCF concentrations of 4900 ng L^{-1} were detected, and the surface water in Germany exhibited a maximum concentration of 1030 ng L^{-1} [4]. DCF residues have been detected in surface waters across European countries, prompting the European Commission to establish maximum allowable concentrations. For inland surface waters (rivers, lakes, and related bodies), the annual average limit is set at 0.1 µg L^{-1}, while other surface waters have a limit of 0.01 µg L^{-1} [6]. These findings highlight the widespread occurrence of DCF and the need to monitor its concentrations in water bodies due to its potential ecological impact and implications for water quality standards.

To address these challenges, various methods have been developed to effectively remove pollutants from water streams [7]. Among these, biosorption has gained significant attention. Biosorption involves the use of biodegradable materials as adsorbents in an adsorption process [8]. This approach offers a simple, cost-effective, and environment-friendly solution for pollutant removal. One notable advantage is that it does not require the addition of nutrients, and the recovery of both the adsorbent and pollutant is possible [9].

Moringa oleifera (MO), a member of the Moringaceae genus, is a tropical plant renowned for its various beneficial properties [10]. It is globally recognized for its coagulant, antimicrobial, and medicinal properties as well as its high nutritional value. MO is rich in proteins, vitamins, carbohydrates, fiber, and fatty acids, making it a valuable resource [1,11]. In the field of wastewater treatment, Moringa oleifera has garnered significant attention. The use of MO seeds or powders obtained from their pods has shown promising results in reducing water turbidity, controlling bacterial presence, and achieving high removal percentages of suspended solids [12]. Its effectiveness as a natural coagulant makes it a sustainable and cost-effective alternative for water treatment.

The primary objective of this study was to elucidate the underlying mechanisms governing the drug adsorption process. To achieve this, a comprehensive investigation was conducted to assess the influence of the pH of the solutions and analyze the kinetics of adsorption. By examining the effects of pH and studying the adsorption kinetics, we aim to gain a deeper understanding of the factors and processes involved in drug adsorption. This research will contribute to expanding our knowledge of the behavior of drugs and provide valuable insights into their efficient removal and potential applications in water treatment.

2. MATERIALS AND METHODS

2.1 Preparation of biosorbent

The Moringa oleifera shells (Figure 1) were collected from Luanda, Angola, Africa. Subsequently, the shells were dried in an oven at 30°C for one day and then pulverized using IKA A11 grinding equipment. Figure 2 illustrates the separation of the MO powder through a series of sieves with different diameters (0.425, 0.250, 0.106, 0.075, and less than 0.075 µm). For each test, particles in the size range of 0.106–0.205 µm were used.

Figure 1 Moringa oleífera shells used in laboratory experiments.

Figure 2 Granulometric analysis of Moringa oleífera.

2.2 Surface charge characterization of the adsorbent

A mass of M. oleifera (100 mg) was mixed with 50 ml of distilled water in a Shaking Incubator at a constant stirring speed of 150 rpm and a temperature of 25°C. The pH of the solution was adjusted using 0.1 M HCl and 0.1 M NaOH solutions, which were carefully measured using a burette and a pH meter from HANNA Instruments. The experimental setup ensured precise control over the pH conditions for accurate determination of the adsorbent surface charge.

2.3 pH effect

pH plays a critical role in the biosorption process as it not only alters the chemical properties of the pharmaceutical solution but also influences the activation of adsorbent sites, thereby affecting its

removal capacity. To investigate this, the study was conducted within a pH range of 2-10, with pH values of 2, 5, 7, 8, and 10. Other parameters, such as the volume of the solution (50 ml), initial concentration of the antibiotic (1 mg L^{-1}), dosage of the adsorbent (2 g L^{-1}), stirring speed (150 rpm), and temperature (25°C), were kept constant throughout the experiment. By systematically varying the pH, we aimed to evaluate its impact on the biosorption process and gain insights into the optimal pH conditions for the efficient removal of pharmaceutical compounds.

2.4 Biosorption kinetic

A pre-equilibrium kinetic experiment was conducted to determine the time required to reach equilibrium for the batch reaction, which is crucial for studying the sorption isotherms. The experiment was carried out using 50 ml Erlenmeyer flasks containing a solution of 1 mg L^{-1} of Diclofenac (DCF) and 100 mg of the adsorbent. The adsorption process was performed under continuous stirring at 150 rpm, constant temperature of 25°C, and pH of 2.

Samples were collected from Erlenmeyer flasks at seven different time intervals (5, 10, 20, 30, 60, 90, and 120 min). The samples were subsequently centrifuged at 5000 rpm for 15 min and filtered using syringes with 45 µm filters. All experiments were conducted in duplicate to ensure the accuracy and reliability of the results.

To quantify the amount of pharmaceutical compounds present in the solution and evaluate the biosorption removal efficiency, the samples were analyzed using high-performance liquid chromatography with a diode-array detector (HPLC-DAD). This analytical technique allowed for accurate measurement and characterization of diclofenac concentration, providing valuable insights into biosorption efficiency.

The adsorption capacity ofMO, q_t (mg g^{-1}) was obtained using Eq. 1:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

Where C_0 is the initial diclofenac concentration (mg L^{-1}), C_t is the diclofenac concentration (mg L^{-1}) in the solution at timet, V is the volume of the solution (mL) and m is the adsorbent mass (mg) [13].

In this study, Pseudo-first-order, Pseudo-second order and Intraparticle Diffusion models were fitted to the experimental data.

Pseudo-first-order model:

$$q_t = q_e(1 - e^{K_1 t}) \quad (2)$$

Where q_t and q_e are the amounts of diclofenac adsorbed per unit mass of MO (mg g^{-1}) at time t and equilibrium, respectively; K_1 is the first order adsorption rate constant (min^{-1}) [14].

Pseudo-second-order model:

$$q_t = \frac{q_e^2 K_2 \cdot t}{1 + q_e \cdot K_2 \cdot t} \quad (3)$$

Where K_2 is the adsorption rate constant (g mg^{-1} min^{-1}) [14].

Intraparticle diffusion model:

$$q_t = K_p t^{1/2} + c \quad (4)$$

Where K_p is the Intraparticle diffusion rate constant (g mg^{-1} $min^{-1/2}$) and c is a constant for any experiment (mg g^{-1}) [15].

3. RESULTS AND DISCUSSION

3.1 Determination of adsorbent's surface charge

Investigating the surface charge of the adsorbent provides valuable insights into the interaction between Moringa oleifera and pharmaceutical compounds, particularly at the tested pH values. Figure 3 clearly illustrates that the surface charge of the adsorbent is positive at pH values below 6, whereas it becomes negative at pH values above 6. This information enhances our understanding of the electrostatic forces and interactions involved in the biosorption process between adsorbents and pharmaceuticals. By determining the surface charge, we gained valuable knowledge about the behavior and potential mechanisms of Moringa oleifera in the adsorption of pharmaceutical compounds under different pH conditions.

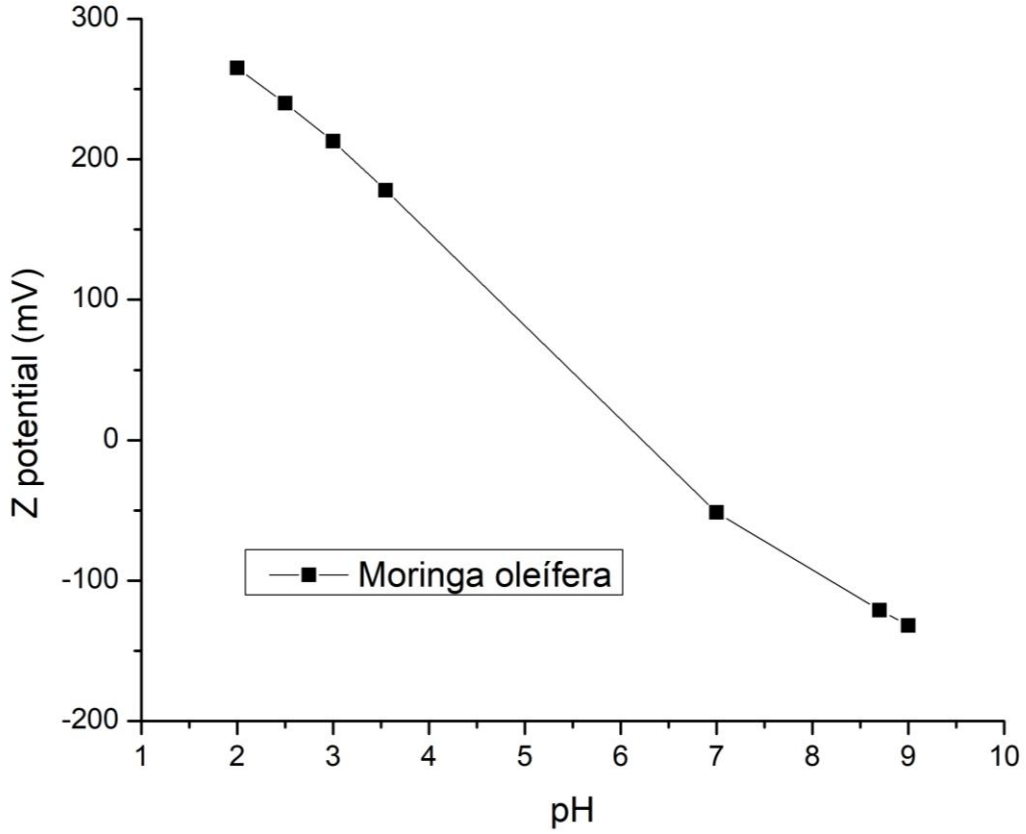

Figure 3 Zeta potential of Moringa Oleífera shells

Based on the work of Araujo et al. (2018) The surface charge of anti-inflammatory drugs is well established to be negative [16]. This suggests a strong electrostatic attraction between Moringa oleifera (MO) and the drug's surface when the pH is below 6, while significant electrostatic repulsion occurs at pH values above 6. In the adsorption of the drug, the acidic pH range, particularly at pH 2, demonstrated the most favorable conditions, resulting in the highest percentage of removal. This indicates the significant potential of the adsorbent and the strong affinity between the solute and the MO. Conversely, at the initial pH of the adsorbent (pH 8), a removal percentage of approximately 10% was achieved, highlighting the substantial influence of pH on the adsorption process and the complex interactions between the two surfaces.

3.2 pH effect on biosorption

pH plays a crucial role in the removal of diclofenac, as shown in Figure 4.

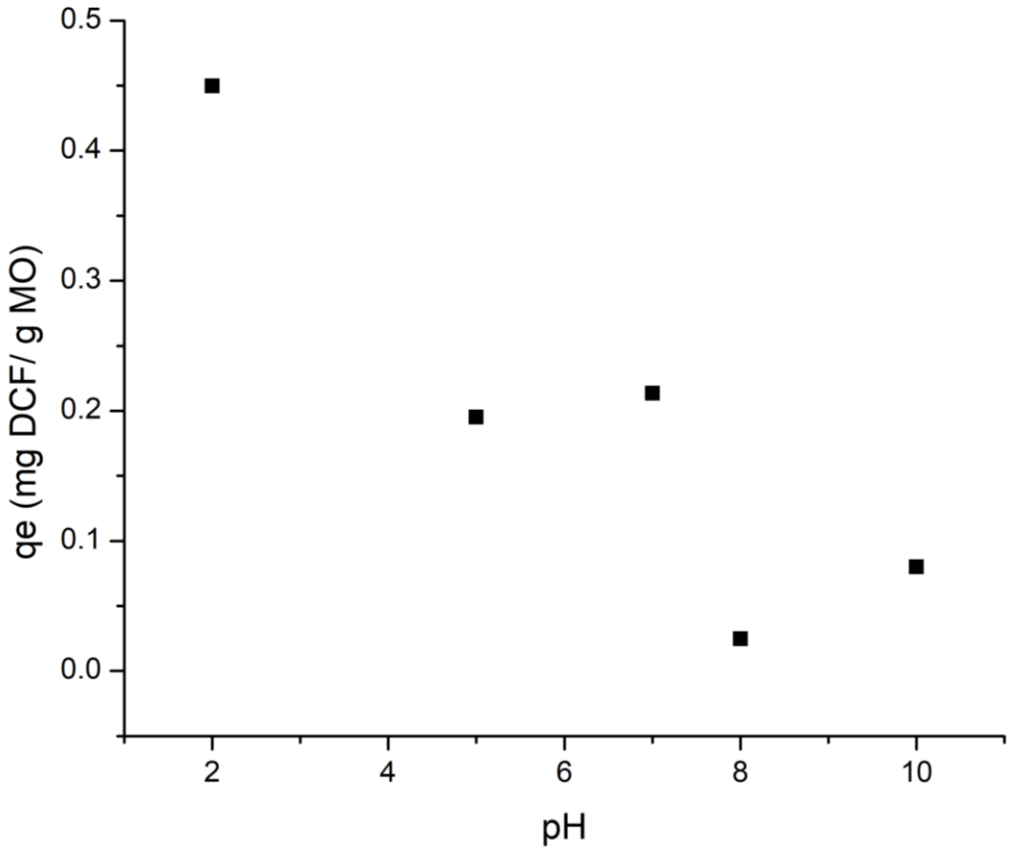

Figure 4 Effect of pH on DCF adsorption.

The adsorption capacity of the adsorbent decreased with an increase in pH. The lowest removal percentage was observed at pH 8 (4.8%), whereas the highest removal percentage was achieved at pH 2 (87.3%). This behavior can be attributed to the negative charge on the surface of diclofenac at low pH, which interacts favorably with the positively charged MO surface, enhancing the adsorption process. Conversely, at an alkaline pH, both surfaces become negatively charged, resulting in significant electrostatic repulsion between them, leading to a lower adsorption capacity.

Based on these results, it can be concluded that Moringa oleifera is an effective adsorbent for the removal of diclofenac from water, with a removal capacity of 0.4497 mg DCF per gram of MO. These findings demonstrate the potential of Moringa oleifera as a viable solution for the removal of diclofenac, highlighting its suitability for water treatment applications and ability to mitigate the presence of pharmaceutical contaminants in aquatic environments.

3.3 Biosorption kinetic study

Figure 5 illustrates the kinetics of the Diclofenac (DCF) adsorption. It can be observed that a removal percentage of nearly 75% was achieved after approximately 90 minutes of adsorption. This significant removal efficiency demonstrates that Moringa oleifera shells are a promising option for the removal of anti-inflammatory compounds from water.

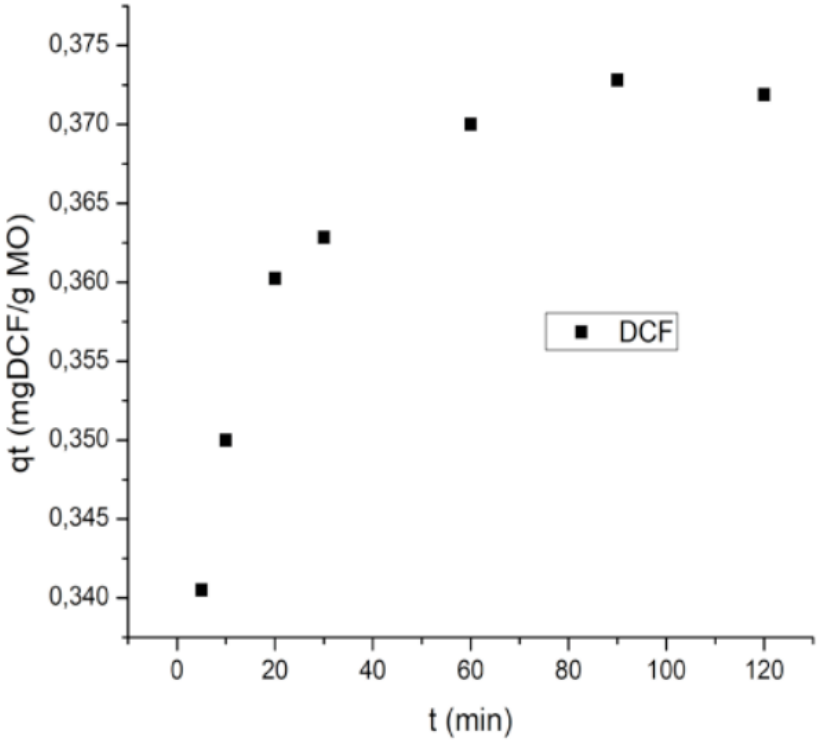

Figure 5 Biosorption capacity of DCF by Moringa oleífera.

To study the adsorption kinetics, various models, including pseudo-first-order, pseudo-second-order, and Intraparticle Diffusion models, were employed. Kinetic parameters, such as rate constants, equilibrium adsorption capacities, correlation coefficients, and F-values, were determined and are summarized in Table 1. These parameters provide valuable insights into the adsorption mechanism, and can be used to evaluate the effectiveness of the adsorption process.

The kinetic data for the DCF adsorption process were analyzed using different models, and it was found that the pseudo-second-order model provided the best fit (Figure 6). This suggests that the adsorption process is likely governed by chemisorption, indicating a strong chemical interaction between DCF and the MO surfaces. The Pseudo-second-order model is commonly associated with chemisorption processes, where the rate-limiting step involves the sharing or exchange of electrons between the adsorbent and adsorbate. This finding further supports the notion that Moringa oleifera shells are effective in adsorbing diclofenac from aqueous solutions through a chemically driven mechanism.

Table 1 Kinetic parameters of Pseudo-first order, Pseudo-second order, and Intraparticle Diffusion models for diclofenac biosorption.

Model	**Rate Constant**	**Eq. Adsorpt. Capacity (q_e)**	**R^2**	**F-value**	**Prob>F**
Pseudo-first order	0.5231 min^{-1}	0.3653 mg g^{-1}	0.5452	6823	$4.93*10^{-9}$
Pseudo-second order	5.31 min^{-1}	0.3718 mg g^{-1}	0.9311	45070	$4.40*10^{-11}$
Intraparticle Diffusion	0.0172 mg g^{-1} $min^{-1/2}$		0.8933	29087	$1.3*10^{-10}$

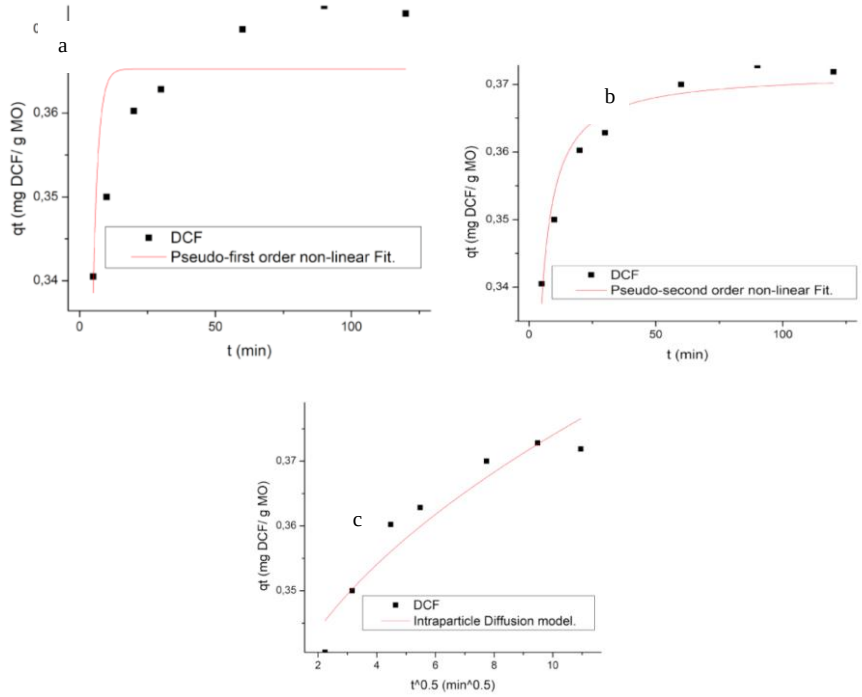

Figure 6 Kinetics for Diclofenac biosorption by Moringa oleífera; Pseudo-first order (a), Pseudo-second order (b), Intraparticle Diffusion model (c).

3.3 Biosorption mechanism

Understanding the adsorption mechanism is crucial for gaining insights into the adsorption process. The adsorption kinetics of diclofenac (DCF) removal suggest that it is governed by a chemisorption mechanism. The process exhibits strong pH dependence, which significantly influences the interactions between DCF and the adsorbent.

At pH 2, the DCF surface carried a negative charge, whereas the adsorbent (MO) surface was positively charged. This creates favorable electrostatic interactions between the negative ions of DCF (O- and OH) and the positive ions on the MO surface (amines and aromatic compounds). This strong electrostatic attraction facilitates the adsorption process.

As the pH was increased to 5, the removal capacity started to decrease. While the MO surface remained positively charged, DCF also acquired positive charges, leading to a small electrostatic repulsion between the two compounds. The amine group of DCF can interact with oxygen groups such as hydroxyls and carbonyls on the MO surface. In addition, the negative chloride (Cl) ions of DCF may form bonds with the aromatic groups (CH) of the adsorbent.

In the pH range of 7–10, both the adsorbent and DCF surfaces become negatively charged, resulting in strong electrostatic repulsion and a decrease in adsorption capacity. Despite this, there may still be some interactions between the positive charge of the amine group in DCF and the negative ions from MO. However, the repulsion between the carbonyl and hydroxyl groups of the anti-inflammatory and functional groups of the adsorbent became stronger and more significant, ultimately reducing the overall adsorption capacity.

Overall, these findings shed light on the intricate interplay among pH, surface charges, and functional groups, providing a deeper understanding of the adsorption mechanism of diclofenac by Moringa oleifera.

4. CONCLUSIONS

The surface charge of the adsorbent was influenced by the solution pH, which was negative for pH values above 6 and positive for pH values below 6. This highlights the complex interactions between the adsorbate (DCF) and adsorbent (Moringa oleifera) surfaces.

The kinetic study revealed that a significant removal percentage of approximately 75% was achieved within approximately 90 min, indicating an acceptable adsorption capacity of Moringa oleífera. To further investigate the adsorption capacity, future work should focus on extending the contact time between the adsorbent and adsorbate (DCF).

pH dependence of the DCF solution was observed, with the lowest removal percentage obtained at pH 8 (4.8%) and the highest at pH 2 (87.3%). This suggests that Moringa oleífera exhibits a favorable affinity for DCF. However, further research is needed to explore the potential of biosorption as a nonconventional method for pharmaceutical removal, as it holds promise for future applications.

The findings of this study highlight the pH-dependent nature of DCF adsorption by Moringa oleífera and its potential as an effective adsorbent. Future investigations should focus on optimizing the adsorption process and exploring wider applications of biosorption for pharmaceutical removal.

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5. REFERENCES

1. V. Gomez, K. O. Angulo, "Review of characteristics and uses of the plant Moringa oleífera", Investigación y Desarrollo, pp. 309-330, 2014.
2. G. Dantas, M. Sommer, R. Oluwasegun, G. Church, "Bacteria Subsisting on Antibiotics", Science, vol. 320, pp. 100-103, 2008.
3. K. Gazdová, E. Kubiňáková, J. Híveš, T. Mackuľak, "Degradation of anti-inflammatory drug diclofenac in sewage water", Acta Chimica Slovaca, vol. 10, no. 1, pp. 1-5, 2017.
4. L. Lonappan, S. B. Kaur, R. Das Kumar, M. Verma, R. Y. Surampalli, "Diclofenac and its transformation products: Environmental occurrence and toxicity - A review", Environ. Int., vol. 96, pp. 127-138, 2016.
5. N. Vieno, M. Sillanpää, "Fate of diclofenac in municipal wastewater treatment plant — A review", Environ. Int., vol. 69, pp. 28-39, 2014.
6. D. O. COUNCIL, "Environmental Quality Standards of chemical substances", European Commission, Brussels, 2012.
7. L. Lonappan, T. Rouissi, Y. Liu, S. B. Kaur, R. Y. Surampalli, "Removal of diclofenac using microbiochar fixed-bed column bioreactor", Environ. Chem. Eng., vol. 7, no. 1, pp. 1-8, 2019.
8. A. L. Estrella, "Adsorción de cadmio, hierro y plomo en agua artificial utilizando Moringa oleifera Lam", Universidad San Francisco de Quito USFQ, Colegio de Ciencias e Ingenierías, Quito, Colombia, 2017.
9. T. Tovar, Á. V. Ortiz, L. G. Jaraba, "Adsorption of heavy metals in wastewater using biological materials", Tecnol., vol. 18, no. 34, pp. 109-123, 2015.
10. A. Pérez, T. Sánchez, N. Armengol, F. Reyes, "Characteristics and potential of Moringa oleifera, Lamark", Pastos y Forrajes, vol. 33, no. 4, pp. 1-16, 2010.
11. R. Abbas, F. E. Seleman, A. A. Fadlelmula, "Nutritional Values of Moringa oleifera, Total Protein, Amino Acid, Vitamins, Minerals, Carbohydrates, Total Fat and Crude Fiber, under the Semi-Arid Conditions of Sudan", J. Microbiol. Biochem. Technol., vol. 10, no. 2, pp. 56-58, 2018.
12. A. Martín, "Potenciales aplicaciones de Moringa oleifera. Una revisión crítica", Pastos y Forrajes, vol. 36, no. 2, pp. 137-149, 2013.
13. W. Boulaiche, B. Hamdi, M. Trari, "Removal of heavy metals by chitin: equilibrium, kinetic and thermodynamics studies", Appl. Water Sci., vol. 39, 9:39, 2019.
14. J. P. Simonin, "On the comparison of pseudo-first order and pseudo- second order rate laws in the modeling of adsorption kinetics", Chem. Eng. J., vol. 300, pp. 254-263, 2016.
15. J. Wang, X. Guo, "Rethinking of the intraparticle diffusion adsorption kinetics model: interpretation, solving methods and applications", Chemosphere, vol. 309, 136732, 2022.
16. L. Araujo, C. Bezerra, L. Cusioli, M. Silva, L. Nishi, R. Gomes, "Moringa oleifera biomass residue for the removal of pharmaceuticals from water", J. Environ. Chem. Eng., vol. 6, no. 6, pp. 7192-7199, 2018.