Opportunities and Challenges in Sustainability
https://www.acadlore.com/journals/OCS

Evaluation of Activated Carbon as an Alternative Treatment for Agrochemical-Contaminated Water in Rural Areas

Patricia Aline Bressiani[1], Geiciane Locatelli Alves[1], Inara Giacobbo de Marco[1], Mariana Tonello Biffi[1], Sabrina Ishikawa[1], Vilmar Steffen[2], Fernando César Manosso[3], Eduardo Michel Vieira Gomes[4], Ticiane Sauer Pokrywiecki[2], Ana Paula de Oliveira Schmitz[2*], Elisângela Düsman[5]

[1] Chemical Engineering Course, Federal University of Technology-Parana (UTFPR), 85602-863 Francisco Beltrão, Brasil
[2] Academic Department of Engineering, Federal University of Technology-Parana (UTFPR), 85602-863 Francisco Beltrão, Brasil
[3] Academic Department of Agricultural Sciences, Federal University of Technology-Parana (UTFPR), 85602-863 Francisco Beltrão, Brasil
[4] Academic Department of Physics, Federal University of Technology-Parana (UTFPR), 85602-863 Francisco Beltrão, Brasil
[5] Academic Department of Chemistry and Biology, Federal University of Technology-Parana (UTFPR), 85602-863 Francisco Beltrão, Brasil

[*] Correspondence: Ana Paula de Oliveira Schmitz (anapoliveira@utfpr.edu.br)

Received: 10-09-2024 **Revised:** 12-12-2024 **Accepted:** 12-21-2024

Citation: Bressiani, P. A., Alves, G. L., de Marco, I. G., Biffi, M. T., Ishikawa, S., Steffen, V., Manosso, F. C., Gomes, E. M. V., Pokrywiecki, T. S., de Oliveira Schmitz, A. P., & Düsman, E. (2024). Evaluation of activated carbon as an alternative treatment for agrochemical-contaminated water in rural areas. *Oppor Chall. Sustain.*, *3*(4), 247-255. https://doi.org/10.56578/ocs030404.

Abstract: The excessive application of agrochemicals has resulted in significant workplace exposure for agriculturists and environmental interaction for the general public, particularly in communities adjacent to agricultural zones. Such exposure is associated with detrimental health effects, including mutagenic and cytotoxic impacts. Agrochemical contamination frequently occurs through water, especially in rural villages where conventional water treatment systems are not designed to address these specific contaminants. The efficacy of activated carbon was investigated in this study as an adsorbent for the removal of 2,4-dichlorophenoxyacetic acid (2,4-D) from contaminated water. The concentration of 2,4-D in water samples was quantified using ultraviolet-visible (UV-Vis) spectroscopy at a wavelength of 283 nm. Preliminary adsorption experiments identified pH 2 as the optimal condition for 2,4-D uptake. The adsorption kinetics were best described by the Elovich model, with an equilibrium time of 480 minutes. Equilibrium studies revealed that three isotherm models—Redlich-Peterson, Temkin, and Toth—effectively represented the experimental data, with a maximum adsorption capacity of 252.8 mg/g. The findings underscore the potential of activated carbon as a cost-effective and straightforward treatment method for the removal of 2,4-D from drinking water, particularly in rural areas lacking access to advanced water treatment infrastructure.

Keywords: Agrochemicals; 2,4-Dichlorophenoxyacetic acid; Water contamination; Activated carbon; Adsorption

1. Introduction

2,4-D is a weed control agent that ranks among the extensively used agrochemicals in agriculture. Its broad application worldwide aims to prevent the growth of unwanted weeds and broadleaf pests, thereby increasing crop yields for maize, soybeans, rice, wheat, and other crops (Georgin et al., 2021; Orduz et al., 2021; Song, 2014). 2,4-D was classified by the International Agency for Research on Cancer (IARC) as a group 2B substance (WHO IARC, 2004), indicating it is possibly carcinogenic to humans. Additionally, Brazil's National Health Surveillance Agency classified it as extremely toxic (class I) (ANVISA, 2003).

The use of 2,4-D has raised significant environmental concerns, particularly regarding water pollution, due to

its high aquatic persistence. This persistence poses threats to the health of humans, animals, and plants (Islam et al., 2018; Salman & Hameed, 2010).

Studies, such as the one conducted by Bressiani et al. (2022), have highlighted the cytotoxic and mutagenic risks associated with 2,4-D exposure. Centering on Vila Rural Água Viva, a rural community situated in rural areas of the Francisco Beltrão City in the state of Paraná, Brazil, those researchers established a correlation between environmental exposure to this herbicide and mutagenic and cytotoxic alterations in human cells through the buccal micronucleus cytome test. In this village, water is sourced from an artesian well located near agricultural areas, with an additional surface water source used for livestock watering and vegetable irrigation. Both water sources were found to contain traces of 2,4-D.

Herbicides play a crucial role in improving crop yields. In Brazil, 2,4-D is authorized for application during both pre- and post-emergence stages to manage weeds in various crops, including rice, oats, coffee, sugarcane, rye, barley, maize, pasture, soybeans, sorghum, and wheat. Vila Rural Água Viva is surrounded by agricultural lands primarily devoted to the cultivation of yearly agricultural products, which often rely heavily on the application of agrochemicals (Bressiani et al., 2022).

Given the health and environmental risks associated with agrochemical contamination, particularly 2,4-D, the development and implementation of effective water treatment methods are imperative (Georgin et al., 2021). Conventional water treatment systems employed by sanitation companies are often insufficient to remove these specific pollutants, underscoring the need for alternative solutions. Adsorption has garnered significant attention for its operational simplicity, cost-effectiveness, straightforward design, low energy requirements, broad range of applications, and potential for recycling (Tyagi & Anand, 2024). Adsorption using activated carbon has emerged as a promising method, owing to its high surface area and porosity (Jawad et al., 2020). Adsorbents derived from agro-waste are capable of removing organic molecules responsible for taste, odor, and toxicity from wastewater (Scheufele et al., 2020). Biosorbents can also be employed to remove pharmaceuticals (Alberti et al., 2024; Módenes et al., 2021; Xue et al., 2024; Wang et al., 2024), heavy metals (Hashem et al., 2024; Ren et al., 2022; Steffen et al., 2015; Suzaki et al., 2023), dyes (Aniagor et al., 2024; Gita et al., 2023; Scheufele et al., 2015), herbicides (Alberti et al., 2023), and more. Furthermore, activated carbon can be produced from coconut shells, an abundant agroindustrial waste, offering a sustainable and cost-effective approach (Freitas et al., 2019).

Georgin et al. (2021), Lazarotto et al. (2021), Orduz et al. (2021), and Rambabu et al. (2023) also assessed the depletion of the 2,4-D via the adsorption process using agroindustrial waste, demonstrating its potential for treating contaminated water containing this pollutant. Furthermore, due to the nature of this process, the possibility of implementing water treatment systems in rural villages, operated by local residents, is highlighted. Such an approach could significantly improve drinking water quality in these areas.

In the context of environmental pollution by agrochemicals like 2,4-D, this study aims to propose an alternative water treatment solution for human consumption in rural villages supplied by artesian wells. In these regions, water treatment is typically not conducted by public water supply companies, and specific processes for agrochemical removal are lacking in water treatment plants across Brazil. As a result, the water treatment systems in these areas must be low-cost and easy to operate to facilitate implementation directly within the rural communities. Therefore, this study focuses on investigating the decontamination of water containing 2,4-D employing activated carbon derived from palm coconut shells, a sustainable adsorbent sourced from agricultural by-products.

2. Materials and Methods

2.1 Preparation of the 2,4-D Herbicide Solutions

2,4-D (active compound of the herbicide) was obtained from agricultural producers in rural areas of a small town near Francisco Beltrão, with a concentration of 806 g L^{-1}. The solution of 2,4-D prepared for analysis was obtained by dissolving the active ingredient in Milli-Q water to achieve the desired concentration for each test.

2.2 Adsorption Tests

Granular activated carbon from palm coconut shell (Bahia Carbon brand) was used as the adsorbent. After the adsorption tests that were carried out in Erlenmeyer flasks of 125 mL adding approximately 0.10 g of adsorptive material and a volume of 50 mL of the herbicide solution (initial concentration 100 mg/L), the adsorbent (solid phase) was removed from the solution (liquid phase) using vacuum filtration using a 0.22 μm PVDF membrane. All adsorption tests were conducted in batch mode and duplicated.

UV-Vis spectroscopy was used to measure 2,4-D concentration. This technique was suitable due to the high concentrations of the agrochemical in the adsorption tests, which allowed for a more robust, lower-cost analysis with guaranteed accuracy, as demonstrated in previous studies (Njoku et al., 2015; Rambabu et al., 2023; Salman & Hameed, 2010). To validate the accuracy of the technique, the concentration values obtained from the HPLC

calibration curve and those measured using UV-V is spectrophotometry (data not shown) were compared, yielding consistent results.

2.2.1 Adsorption preliminary tests

Preliminary tests were conducted to determine the pH value that benefits the 2,4-D adsorption for use in the equilibrium and kinetic tests. For this purpose, tests were performed with initial pH values of 2, 3, 5, and 7 at room temperature (25ºC). The adsorption tests were conducted in batch mode using Erlenmeyer flasks of 125 mL, with the addition of approximately 0.10 g of adsorptive material and 50 mL of the 2,4-D solution (initial concentration 100 mg/L).

The contents of the Erlenmeyer flask were agitated at 100 rpm for eight hours. Then the samples were filtered and analyzed using a UV-Vis spectrophotometer at a maximum wavelength of 283 nm. The concentration of the adsorbed herbicide can be determined using the mass balance, which is represented by Eq. (1).

$$q = \frac{(C_0 - C)V}{m} \tag{1}$$

where, q is the adsorbed herbicide concentration (mg g^{-1}), C_0 and C are concentrations in the liquid phase at the start and the end of the process, respectively, i.e., the times when the contact between the phases begins and ends (mg L^{-1}), V is the volume of the herbicide solution used in each batch experiment (L), and m is the mass of the adsorptive material used in each run (g).

After the preliminary tests were conducted to define adequate pH conditions, the kinetic tests aimed at determining the equilibrium time of the process under study and finally equilibrium tests were performed to identify the isothermal behaviour of the adsorption in equilibrium and enable analyzing features like maximum adsorption capacity.

2.2.2 Adsorption kinetic tests

To study the kinetics of adsorption, the adsorption tests were performed in batch with a herbicide solution at an initial concentration of 100 mg L^{-1} using a proportion of 0.10 g of adsorptive material in 50 mL of herbicide solution. The mixture was kept under agitation at 100 rpm and at room temperature (25ºC) for contact times of 0, 3, 5, 10, 15, 30, 45, 60, 75, 90, 120, 180, 240, 360, 480, and 1440 minutes. These time points were carefully selected to ensure a comprehensive understanding of the kinetic profile, capturing the rapid concentration changes at the beginning of the experiment and the slower variations near equilibrium. After each contact time, the adsorptive material was separated from the solution by filtration, and the solution concentration was measured by absorbance at 283 nm.

2.2.3 Adsorption equilibrium tests

For the equilibrium test, herbicide solutions were obtained by diluting the active compound in Milli-Q water at concentrations ranging from 10 to 800 mg L^{-1}. These concentration points were carefully selected to provide a comprehensive understanding of the adsorption equilibrium profile up to the saturation of the adsorbent. The adsorption tests, conducted to study the adsorption equilibrium, were performed in batch using a proportion of 0.10 g of adsorptive material in 50 mL of herbicide solution. During the tests, the contents of the Erlenmeyer flask were agitated at 100 rpm and maintained at room temperature (25ºC) for eight hours. After each test, the adsorptive material was separated from the solution by filtration, and the solution concentration was measured by the UV-Vis spectrophotometer at a wavelength of 283 nm.

3. Results and Discussion

3.1 Adsorption Preliminary Tests

In the present study, the influence of pH on the adsorption of 2,4-D was initially examined. According to Njoku et al. (2013), the pH of the solution containing the adsorbate plays a crucial role in influencing the adsorption process. As summarized in Table 1, no substantial difference was observed in the 2,4-D removal capacity values for the tests performed with initial solution pH values of 2 and 3. Therefore, pH 2 was chosen for further experiments, as an increase in pH was found to reduce the removal capacity, with the process being favored at acidic pH values. Rambabu et al. (2023) reported the low pKa value of 2,4-D (2.81), which leads to high mobility at natural pH levels in its anionic form.

Table 1. Influence of pH on the 2,4-D uptake, adapted from Bressiani et al. (2023)

Initial pH	Initial Concentration (mg L^{-1})	Final Concentration (mg L^{-1})	q (mg g^{-1})
2	82.7 ± 1.0	11.1 ± 1.1	35.6 ± 0.6
3	89.7 ± 1.2	16.1 ± 0.5	36.5 ± 0.2
5	94.4 ± 2.1	37.2 ± 6.4	28.4 ± 3.1
7	95.2 ± 1.2	40.7 ± 0.4	27.1 ± 0.2

According to Aksu & Kabasakal (2004), Njoku et al. (2013), and Salman & Hameed (2010), pH 2 also favored the 2,4-D uptake. Under higher pH conditions, 2,4-D dissociates more extensively, remaining in its ionized form (2,4-dichlorophenoxyacetate ion), which leads to repulsion or dispersion between the 2,4-D ions and the adsorbent surface, thus decreasing the adsorption efficiency. Furthermore, at high pH, the increased mobility of hydroxyl ions can compete with the ionized form for active adsorption sites (Diaz-Flores et al., 2006). Salman & Hameed (2010) suggested that the increase in removal capacity is influenced by the surface properties of the adsorptive material and the structure of the agrochemicals. Therefore, in an acidic medium, the uptake of the herbicide occurs more rapidly than in a basic medium.

3.2 Adsorption Kinetic Assays

Subsequently, the adsorption kinetics tests were conducted under the optimal operational conditions determined from the preliminary pH test (pH 2), with the temperature kept constant at 25ºC and the agitation speed at 100 rpm. From the kinetic data, it was found that equilibrium was achieved after roughly 480 minutes of interaction between the adsorptive material and the 2,4-D liquid solution (Figure 1), which was used as the contact time for the other tests. Among the various kinetic models, the data were evaluated using Elovich, pseudo-first-order and pseudo-second-order models, as these are the most widely used and well-established models in the literature to describe adsorption processes. The pseudo-first-order and pseudo-second-order models are particularly popular due to their simplicity and ability to describe different adsorption behaviors, such as chemisorption and physisorption. The Elovich model, on the other hand, is often applied to systems with heterogeneous adsorbent surfaces, which may better capture the multifaceted nature of the adsorption process in this study. The estimated kinetic model parameters, along with the corresponding model fits to the experimental data, are shown in Table 2 and illustrated in Figure 1.

In the discussion of the kinetic models, the Elovich model best fitted the experimental data, presenting the highest coefficient of determination value (0.974). This model is commonly applied to systems where chemisorption occurs, particularly when adsorption takes place on heterogeneous surfaces. In these systems, the adsorption rate decreases exponentially as more adsorbate accumulates on the surface. The Elovich equation accounts for the initial rapid adsorption and the gradual slowing down as the adsorption sites become occupied, which is characteristic of many adsorption processes.

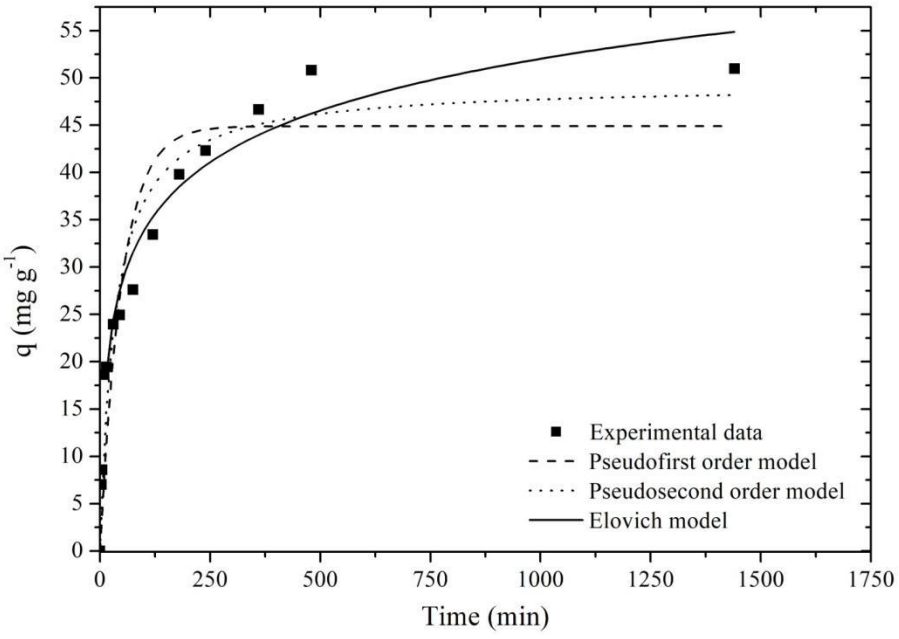

Figure 1. 2,4-D kinetic behavior (pH 2, 25°C, agitation of 100 rpm)

Table 2. Parameters fitted of kinetic models to experimental adsorption data, adapted from Bressiani et al. (2023)

Kinetic Models	Parameters	Value of Fit
Pseudo-first-order $q(t) = q_e[1 - exp(-k_1 t)]$	q_e (mg g^{-1}) k_1 (h^{-1}) r^2	44.9 ± 2.7 0.020 ± 0.005 0.877
Pseudo-second-order $q_t(t) = q_e \frac{q_e k_2 t}{q_e(k_2 t) + 1}$	q_e (mg g^{-1}) k_2 (g mg^{-1} h^{-1}) r^2	49.3 ± 2.4 6.0 10^{-4} ± 1.5 10^{-4} 0.939
Elovich $q(t) = \frac{1}{\beta} ln(1 + \alpha\beta t)$	α β r^2	0.093 ± 0.025 7.9 ± 0.4 0.974

The applicability of the Elovich model to the 2,4-D adsorption by activated carbon in this study suggests that the process is controlled by chemical interactions between the adsorptive material and the 2,4-D liquid solution. Specifically, the bond formed during chemisorption is typically stronger than that in physisorption and may involve electrostatic forces or even covalent bonding, which can lead to irreversible adsorption (Qiu et al., 2009; Ruthven, 1984). This is in contrast to the pseudo-first-order and pseudo-second-order models, which assume linear adsorption rates and may not adequately capture the complex interactions present in this system, especially considering the adsorbent surface non-uniformity.

Thus, the Elovich model is more suitable than the other kinetic models for describing the 2,4-D adsorption by activated carbon, as it better reflects the chemical nature of the interaction and the dynamics of adsorption on a heterogeneous surface. This model also indicates that the adsorption process is not simply a diffusion-controlled or monolayer adsorption mechanism, but rather a more complex process involving chemical binding.

3.3 Adsorption Equilibrium Assays

The equilibrium tests were conducted under the optimal operating conditions obtained from the preliminary pH test (pH 2), keeping the adsorbent and adsorbate at room temperature (25ºC) and maintaining a stirring rate of 100 rpm. Among the various adsorption isotherms, five were selected to fit the 2,4-D adsorption equilibrium data—namely, Langmuir, Freundlich, Redlich-Peterson, Temkin, and Toth—since these are the most commonly used. The estimated model parameters and their corresponding fits are shown in Table 3 and Figure 2.

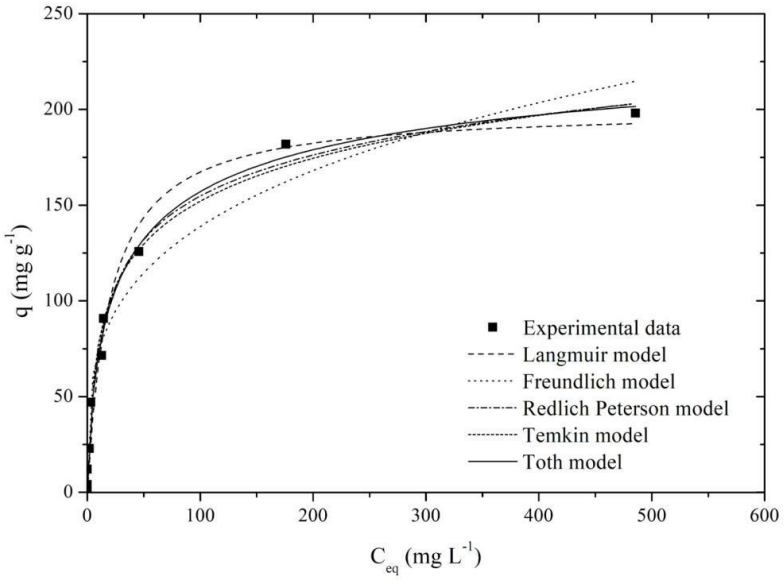

Figure 2. 2,4-D adsorption equilibrium data (pH 2, 25°C temperature, 100 rpm agitation) and isotherm settings

When evaluating the coefficient of determination, it was found that the Redlich-Peterson, Temkin, and Toth isotherms had very similar determination coefficient values (namely, 0.986, 0.986, and 0.988, respectively), indicating that all three isotherms were suitable to represent the experimental data of 2,4-D adsorption on activated carbon.

The Redlich-Peterson isotherm combines features of either the Langmuir and Freundlich isotherms, making it

applicable to both homogeneous and heterogeneous systems (Akpa & Unuabonah, 2011; Qiao et al., 2009). About the Redlich-Peterson isother, one key parameter is β (0.87), which, according to Aksu & Kabasakal (2004), indicates favorable adsorption when β is between 0 and 1, meaning the occurrence of the 2,4-D removal and the realization of equilibrium.

The Langmuir isother, which is widely utilized to represent monolayer adsorption on homogeneous surfaces, showed a saturation capacity (q_{max}) of 200.4 mg g^{-1}. This saturation capacity (also known as the maximum adsorption capacity) represents approximately the maximum amount of 2,4-D that can be adsorbed per unit mass of the adsorbent under ideal conditions. However, the assumption of surface homogeneity inherent to the Langmuir model may be limiting, as materials like activated carbon typically exhibit highly heterogeneous surfaces, with a wide distribution of pore sizes and various surface functional groups. The results for the Freundlich isotherm, which is better suited for heterogeneous systems, indicate a strong interaction between the adsorptive material and the adsorbed compound.

Table 3. Adjusted parameters of evaluated adsorption isotherms, adapted from Bressiani et al. (2023)

Isotherms	Parameters	Fitting Value
Langmuir $q_e = \frac{q_{max} b C_e}{1 + b C_e}$	q_{max} (mg g^{-1})	200.4 ± 9.2
	b (L mg^{-1})	0.051 ± 0.008
	r^2	0.978
Freundlich $q_e = k C_e^{\,1/n}$	k (L g^{-1})	39.0 ± 6.0
	n	3.6 ± 0.4
	r^2	0.959
Redlich-Peterson $q_e = \frac{k_{rp} C_e}{1 + a_{rp} C_e^{\,\beta}}$	k_{rp} (mg g^{-1})	17.8 ± 5.5
	a_{rp} (mg^{-1})	0.2 ± 0.1
	β	0.87 ± 0.05
	r^2	0.986
Temkin $q_e = \frac{RT}{B} ln(k_T C_e)$	B	1.1 ± 0.2
	k_T (L mg^{-1})	32.3 ± 1.7
	r^2	0.986
Toth $q_e = \frac{q_{maxT} b_T C_e}{[1 + (b_T C_e)^{n_T}]^{1/n_T}}$	q_{maxT} (mg g^{-1})	252.8 ± 38.5
	b_T (L mg^{-1})	0.12 ± 0.06
	n_T	0.5 ± 0.1
	r^2	0.988

Based on the outcomes obtained from the Langmuir and Freundlich isotherms, which account for both homogeneous and heterogeneous behaviors, such as Redlich-Peterson and Toth, presented a better fit to the equilibrium data. This suggests that the adsorbent possesses adsorption sites with varying energy levels, highlighting the heterogeneous nature of the activated carbon surface.

Finally, the Temkin isotherm takes into account the interactions between adsorbate and adsorbent material, suggesting that adsorption energy decreases linearly with increasing surface coverage, which is characteristic of heterogeneous systems. The good fit of this model (r^2 = 0.986) reinforces that adsorption on activated carbon is influenced by a combination of factors, including surface heterogeneity and chemical interactions.

The Temkin model considers indirect adsorbate molecule interactions and the decrease in adsorption heat as the adsorbate removal rate increases. Moreover, this model suggests that adsorption is characterized by an homogeneous distribution of binding energies (Ayawei et al., 2017; Daneshvar et al., 2012).

The Toth isotherm is a modification of the Langmuir model, aimed at minimizing the discrepancies between experimental and predicted values. It considers adsorption on a heterogeneous surface (Rangabhashiyam et al., 2014).

Both the Toth and Langmuir isotherms define the maximum adsorption capacity (q_{max} and q_{maxT}, respectively). According to Oliveira et al. (2018), this parameter reflects the number of non-occupied sites on the adsorbent and represents the full saturation of the adsorptive material surface. Based on the Toth isotherm fitting to the experimental data, the saturation capacity of 2,4-D was determined to be 252.8 mg g^{-1}, while the Langmuir isotherm resulted in 200.4 mg g^{-1}.

The second parameter represents the affinity coefficient between the adsorptive material and the adsorbed compound, determined from the Toth (b_T) and Langmuir (b) isotherms. The higher the affinity coefficient value, the stronger the affinity. The affinity coefficient values obtained were 0.124 L mg^{-1} for the Toth isotherm and 0.051 L mg^{-1} for the Langmuir isotherm.

Georgin et al. (2021) evaluated the 2,4-D removal using chalice generated from the production of *Physalis peruviana* fruit chemically treated with acid. The study also determined the optimal conditions for the 2,4-D adsorption at pH 2, with the pseudo-second-order model offering the best quality on the representation of kinetic data. The maximum adsorption capacities observed in their study were 244 and 320 mg g^{-1} for the Langmuir and Toth models, respectively, which are similar to the findings of this study.

Overall, the results of this study highlight the importance of developing affordable and easy-to-implement water treatment methods, particularly for rural communities like Vila Rural Água Viva. In this context, the results for the removal of the 2,4-D agrochemical using activated carbon are promising, with a removal capacity of approximately 250 mg g^{-1}, according to the Toth model (r^2 = 0.988), indicating that equilibrium was achieved after eight hours of contact in a batch experiment.

4. Conclusions

The adsorption process proved to be an efficient method for treating water contaminated with the 2,4-D agrochemical. The Elovich adsorption kinetic model was identified as the best representation of the uptake kinetics, with equilibrium achieved in approximately 480 minutes. Equilibrium studies revealed that three isotherm models—Redlich-Peterson, Temkin, and Toth—effectively described the experimental data, with the Toth model predicting a saturation capacity of 252.8 mg/g. This study highlights the importance of treating drinking water contaminated with agrochemicals and proposes a low-cost, user-friendly method applicable in rural communities. These findings offer a practical solution to improve water quality in areas lacking advanced water treatment infrastructure.

This study primarily focused on evaluating the adsorption performance under specific conditions. However, key factors, such as the influence of temperature on the removal process behavior and the quantification of parameters like thermodynamic ones, were not investigated. Future studies should focus on these aspects to provide a more thorough understanding of the adsorption process. Moreover, experiments using actual rural water samples are essential to evaluate the method's practical effectiveness and uncover potential limitations in real-world scenarios. Another weakness of this study is the absence of practical application guidelines. Implementing the findings in real-world settings would require a well-designed adsorption column system, with provisions for easy adsorbent replacement. However, this demands careful planning and further studies to optimize operational conditions and system scalability.

Data Availability

The data supporting the research findings can be obtained from the corresponding author upon request.

Acknowledgements

We sincerely appreciate the support of the Public Ministry of Labor of the State of Paraná and the Federal Technological University of Paraná, Campus Francisco Beltrão.

Conflicts of Interest

The authors state that they have no conflicts of interest.

References

Akpa, O. M., & Unuabonah, E. I. (2011). Small-sample corrected Akaike information criterion: an appropriate statistical tool for ranking of adsorption isotherm models. *Desalination, 272*(1-3), 20-26. https://doi.org/10.1016/j.desal.2010.12.057.

Aksu, Z., & Kabasakal, E. (2004). Batch adsorption of 2, 4-dichlorophenoxy-acetic acid (2, 4-D) from aqueous solution by granular activated carbon. *Sep. Purif. Technol., 35*(3), 223-240. https://doi.org/10.1016/S1383-5866(03)00144-8.

Alberti, S. W., Hübner, K. V., Busso, C., da Silva, E. A., & Scheufele, F. B. (2023). 2,4-d removal by fish scales-derived carbon/apatite composite adsorbent: Adsorption mechanism and modeling. *J. Mol. Liq., 382*, 121958. https://doi.org/10.1016/j.molliq.2023.121958.

Alberti, S. W., Scheufele, F. B., Steffen, V., & da Silva, E. A. (2024). Adsorption of ciprofloxacin from aqueous media by activated carbon: A review. *Water Conserv. Sci. Eng., 9*(1), 26. https://doi.org/10.1007/s41101-024-00260-0.

Aniagor, C., Aly, M., El-Shazly, A., & El-Shazly, M. (2024). Removal of methylene blue dye from contaminated wastewater using lignocellulosic biomasses: A comparative study. *Waste Manag. Bull., 2*(2), 213-225. https://doi.org/10.1016/j.wmb.2024.05.003.

Agência Nacional de Vigilância Sanitária (ANVISA) (2003). RESOLUÇÃO-RE Nº 899, DE 29 DE MAIO DE 2003. https://bvsms.saude.gov.br/bvs/saudelegis/anvisa/2003/res0899_29_05_2003.html

Ayawei, N., Ebelegi, A. N., & Wankasi, D. (2017). Modelling and interpretation of adsorption isotherms. *J. Chem., 2017*(1), 3039817. https://doi.org/10.1155/2017/3039817.

Bressiani, P. A., Alves, G. L., de Marco, I. G., Biffi, M. T., Ishikawa, S., Manosso, F. C., Gomes, E. M. V., Pokrywiecki, T. S., de Oliveira Schmitz, A. P., & Düsman, E. (2022). Evaluation of genotoxicity and cytotoxicity of inhabitants of vila rural Água viva, brazil, exposed to agrochemicals using the micronucleus buccal cytome assay. *Environ. Toxicol. Pharmacol.*, *96*, 104002. https://doi.org/10.1016/j.etap.2022.104002.

Bressiani, P. A., Gomes, E. M. V., Manosso, F. C., Pokrywiecki, T. S., Düsman, E., & Schmitz, A. P. O. (2023). Avaliação de tratamento com carvão ativado para água de área rural contaminada com agroquímicos. *In VII Workshop De Ciência, Tecnologia E Inovação (VII WCTI), Francisco Beltrão. Paraná, Brasil*, 371–380. https://wcti.fb.utfpr.edu.br/anais/individuais/2023/3_152_anais.pdf

Daneshvar, E., Kousha, M., Sohrabi, M., Khataee, A., & Converti, A. (2012). Biosorption of three acid dyes by the brown macroalga Stoechospermum marginatum: Isotherm, kinetic and thermodynamic studies. *Chem. Eng. J.*, *195-196*, 297-306. https://doi.org/10.1016/j.cej.2012.04.074.

Diaz-Flores, P. E., Leyva-Ramos, R., Guerrero-Coronado, R. M., & Mendoza-Barron, J. (2006). Adsorption of pentachlorophenol from aqueous solution onto activated carbon fiber. *Ind. Eng. Chem. Res.*, *45*(1), 330-336. https://doi.org/10.1021/ie050507o.

Freitas, J. V., Nogueira, F. G., & Farinas, C. S. (2019). Coconut shell activated carbon as an alternative adsorbent of inhibitors from lignocellulosic biomass pretreatment. *Ind. Crops Prod.*, *137*, 16-23. https://doi.org/10.1016/j.indcrop.2019.05.018.

Georgin, J., Franco, D., Netto, M., Allasia, D., Foletto, E., Oliveira, L., & Dotto, G. (2021). Transformingshrubwaste into a high-eficiency adsorbent: Application of physalis peruviana chalice treated with strong acid to remove the 2,4-dichlorophenoxyacetic acid herbicide. *J. Environ. Chem. Eng.*, *9*(1), 104574. https://doi.org/10.1016/j.jece.2020.104574.

Gita, S., Shukla, S. P., Deshmukhe, G., Singh, A. R., & Choudhury, T. G. (2023). Adsorption linked fungal degradation process for complete removal of lanasyn olive dye using chemically valorized sugarcane bagasse. *Waste Manag. Bull.*, *1*(1), 29-38. https://doi.org/10.1016/j.wmb.2023.04.002.

Hashem, M. A., Nayeen, J., Hossain, M. T., & Miem, M. M. (2024). Chromium adsorption on thermally activated adsorbent equipped from waste biomass. *Waste Manag. Bull.*, *2*(1), 239-249. https://doi.org/10.1016/j.wmb.2024.01.009.

Islam, F., Wang, J., Farooq, M., Khan, M., Xu, L., Zhu, J., Zhao, M., Muños, S., Li, Q., & Zhou, W. (2018). Potential impact of the herbicide 2,4-dichlorophenoxyacetic acid on human and ecosystems. *Environ. Int.*, *111*, 332–351. https://doi.org/10.1016/j.envint.2017.10.020.

Jawad, A. H., Abdulhameed, A. S., & Mastuli, M. S. (2020). Acid-factionalized biomass material for methylene blue dye removal: a comprehensive adsorption and mechanism study. *J. Taibah Univ. Sci.*, *14*(1), 305-313. https://doi.org/10.1080/16583655.2020.1736767.

Lazarotto, J., Martinello, K., Georgin, J., Franco, D., Netto, M., Piccilli, D., Silva, L., Lima, E., & Dotto, G. (2021). Preparation of activated carbon from the residues of the mushroom (agaricus bisporus) production chain for the adsorption of the 2,4-dichlorophenoxyacetic herbicide. *J. Environ. Chem. Eng.*, *9*(6), 106843. https://doi.org/10.1016/j.jece.2021.106843.

Módenes, A. N., Bazarin, G., Borba, C. E., Locatelli, P. P. P., Borsato, F. P., Pagno, V., Pedrini, R., Trigueros, D. E. G., Espinoza-Quiñones, F. R., & Scheufele, F. B. (2021). Tetracycline adsorption by tilapia fish bone-based biochar: Mass transfer assessment and fixed-bed data prediction by hybrid statistical-phenomenological modeling. *J. Clean. Prod.*, *279*, 123775. https://doi.org/10.1016/j.jclepro.2020.123775.

Njoku, V., Islam, M., Asif, M., & Hameed, B. (2015). Adsorption of 2,4-dichlorophenoxyacetic acid by mesoporous activated carbon prepared from h3po4-activated langs atempty fruit bunch. *J. Environ. Manag.*, *154*, 138-144. https://doi.org/10.1016/j.jenvman.2015.02.002.

Njoku, V. O., Foo, K., & Hameed, B. (2013). Microwave-assisted preparation of pumpkin seed hull activated carbon and its application for the adsorptive removal of 2,4-dichlorophenoxyacetic acid. *Chem. Eng. J.*, *215-216*, 383-388. https://doi.org/10.1016/j.cej.2012.10.068.

Oliveira, A., Módenes, A., Bragião, M., Hinterholz, C., Trigueros, D., & Bezerra, I. (2018). Use of grape pomace as a biosorbent for the removal of the Brown KROM KGT dye. *Bioresour. Technol. Rep.*, *2*, 92-99. https://doi.org/10.1016/j.biteb.2018.05.001.

Orduz, A., Acebal, C., & Zanini, G. (2021). Activated carbon from peanut shells: 2,4-d desorption kinetics study for application as a green material for analytical purposes. *J. Environ. Chem. Eng.*, *9*(1), 104601. https://doi.org/10.1016/j.jece.2020.104601.

Qiao, S., Hu, Q., Haghseresht, F., Hu, X., & Lu, G. (2009). An investigation on the adsorption of acid dyes on bentonite based composite adsorbent. *Sep. Purif. Technol.*, *67*(2), 218-225. https://doi.org/10.1016/j.seppur.2009.03.012.

Qiu, H., Lv, L., Pan, B., Zhang, Q., Zhang, W., & Zhang, Q. (2009). Critical review in adsorption kinetic models. *J. Zhejiang Univ. Sci.*, *10*(5), 716-724. https://doi.org/10.1631/jzus.A0820524.

Rambabu, K., Bharath, G., Avornyo, A., Thanigaivelan, A., Hai, A., & Banat, F. (2023). Valorization of date palm leaves for adsorptive remediation of 2,4-dichlorophenoxyacetic acid herbicide polluted agricultural runoff.

Environ. Pollut., 316, 120612. https://doi.org/10.1016/j.envpol.2022.120612.
Rangabhashiyam, S., Anu, N., Nandagopal, M., & Selvaraju, N. (2014). Relevance of isotherm models in biosorption of pollutants by agricultural byproducts. *J. Environ. Chem. Eng., 2*(1), 398-414. https://doi.org/10.1016/j.jece.2014.01.014.
Ren, B., Jin, X., Song, X., Li, S., Wang, Y., Wang, H., Li, Q., Wang, S., Wang, X., & Wang, X. (2022). Enhanced Cr(vi) adsorption using chemically modified dormant aspergillus Niger spores: Process and mechanisms. *J. Environ. Chem. Eng., 10*(1), 106955. https://doi.org/10.1016/j.jece.2021.106955.
Ruthven, D. M. (1984). *Principles of Adsorption and Adsorption Process*. John Wiley & Sons, New York.
Salman, J. & Hameed, B. (2010). Adsorption of 2,4-dichlorophenoxyacetic acid and carbofuran pesticides onto granular activated carbon. *Desalination, 256*(1-3), 129-135. https://doi.org/10.1016/j.desal.210.02.002.
Scheufele, F. B., Ribeiro, C., Módenes, A. N., Espinoza-Quiñones, F. R., Bergamasco, R., & Pereira, N. C. (2015). Assessment of drying temperature of sugarcane bagasse on sorption of reactive blue 5G dye. *Fibers Polym., 16*, 1646-1656. https://doi.org/10.1007/s12221-015-5087-2.
Scheufele, F. B., Staudt, J., Ueda, M. H., Ribeiro, C., Steffen, V., Borba, C. E., Módenes, A. N., & Kroumov, A. D. (2020). Biosorption of direct black dye by cassava root husks: Kinetics, equilibrium, thermodynamics and mechanism assessment. *J. Environ. Chem. Eng., 8*(2), 103533. https://doi.org/10.1016/j.jece.2019.103533
Song, Y. (2014). Insight into the mode of action of 2,4-dichlorophenoxyacetic acid (2,4-d) as an herbicide. *J. Integr. Plant Biol., 56*(2), 106-113. https://doi.org/10.1111/jipb.12131.
Steffen, V., Cardozo-Filho, L., Silva, E., Evangelista, L., Guirardello, R., & Mafra, M. (2015). Equilibrium modeling of ion adsorption based on poisson–boltzmann equation. *Colloids Surf. A Physicochem. Eng. Asp., 468*, 159-166. https://doi.org/10.1016/j.colsurfa.2014.11.065.
Suzaki, P. Y. R., Triques, C. C., Munaro, M. T., Steffen, V., Kleinübing, S. J., Klen, M. R. F., Bergamasco, R., & de Matos Jorge, L. M. (2023). Phenomenological modeling and simulation of competitive biosorption of ternary heavy metal systems in a fixed bed column. *Chem. Eng. Res. Des., 196*, 701-710. https://doi.org/10.1016/j.cherd.2023.07.009.
Tyagi, U. & Anand, N. (2024). Sustainable and low-cost biomass derived adsorbents for the removal of toxic contaminants from wastewater: Approaches and future perspective. *Waste Manag. Bull., 2*(2), 308-325. https://doi.org/10.1016/j.wmb.2024.05.010.
Wang, J. B., Li, X. Y., Lan, Y. S., Wang, H. Y., Ma, X. L., Wang, H. B., Xu, H. Y., & Liu, H. Q. (2024). Study on the adsorption mechanism of ciprofloxacin in wastewater by modified fly ash under the coexistence of copper. *J. Environ. Chem. Eng., 12*(6), 114336. https://doi.org/10.1016/j.jece.2024.114336.
World Health Organization International Agency for Research on Cancer (WHO IARC) (2004). WHO IARC. (2004). IARC monographs on the evaluation of carcinogenic risks to humans. *In Tobacco Smoke and Involuntary Smoking. IARC, Lyon, France, 83*, 1-1452.
Xue, H., Deng, L., Kang, D., Zhao, Y., Zhang, X., Liu, Y., Chen, H., Ngo, H. H., & Guo, W. (2024). Advanced biochar-based materials for specific antibiotics removal from hospital wastewater via adsorption and oxidative degradation. *J. Environ. Chem. Eng., 12*(6), 114275. https://doi.org/10.1016/j.jece.2024.114275.