



Removal Of Herbicide from Aqueous Solution Using Granular Activated Carbon: Equilibrium Data and Process Design

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Abstract

2,4-Dichlorophenoxyacetic acid (2,4-D) herbicide is a widely utilized herbicide known to be moderately toxic, have extensive use, poor biodegradability, and lead to contamination of surface and ground waters. The Granular Activated Carbon (GAC) was characterized by its porosity, surface morphology, and availability of functional groups. Type I isotherm was observed in the GAC, indicating microporosity with specific surface area of 832.35 m²/g and pore diameter of 0.899 nm. GAC was evaluated for its ability to adsorb herbicide 2,4-D as the model adsorbate and evaluated the effects of initial concentration, contact time, pH, and activated carbon dosage on the adsorption process. According to the results, 94.01 %, 97.17%, 97.76 %, 98.15%, and 98.2 % of the adsorptive removal were achieved at initial concentrations of 10, 20, 30, 40, and 50 mg/l, respectively. Langmuir and Freundlich isotherm models were used to analyze the adsorption isotherm. It was determined that 2,4-D had a maximum monolayer adsorption capacity of 20.28 mg/g for GAC. Freundlich isotherm model predicted uniform binding energy distribution over heterogeneous surface binding sites for the best fit. The Freundlich model was used to design a batch adsorber capable of removing 2,4-D from effluent solutions of different volumes using the required mass of GAC. Resulting of the achieved results, GAC is a highly effective adsorbent for the removal of 2,4-D from aqueous environments.

Keywords: 2,4-D; GAC; Adsorption; Equilibrium models; Process design

1. Introduction

Globally, access to clean water has become a priority issue. More than one-third of the earth's freshwater is consumed by industrial, agricultural, and domestic activities. The agricultural sector, which accounts for a significant portion of global water withdrawals, contributes greatly to water contamination [1]. Pesticide applications and improper wastewater disposal methods are contaminating water resources and negatively impacting ecosystems and the environment [2]. Among the most widely used pesticides, chlorinated phenoxyacetic acid herbicides account for a larger percentage of global pesticide production [3]. Due to their widespread usage and low soil sorption, these compounds leave ubiquitous residues in the environment, which cause contamination of surface and ground waters [4]. The herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) is commonly used to control broad-leafed weeds in wheat, rice, maize, and aquaculture [5]. It is a low-cost and highly selective herbicide, which makes it an easily accessible and widely available herbicide in the environment, mostly in water bodies [6]. As 2,4-D is moderately toxic and potentially carcinogenic, it causes serious health disorders in both humans and animals [7]. As a result, many countries have enacted strict environmental regulations regarding 2,4-D for drinking water and wastewater treatment [8]. Water quality standards for 2,4-D are set by the World Health Organization at 20 g/l [9, 10]. In light of this, it is necessary to eliminate 2,4-D from the environment. To date, various techniques have been employed to remove 2,4-D, including precipitation, sedimentation, flotation, ion exchange, advanced oxidation processes, ozone oxidation technology, electrochemistry, and biological processes [11]. Several adsorbents such as carbonaceous materials including activated carbons [12-14], layered double hydroxides [15], minerals including bentonite [16], and polymeric materials [17] have been studied for the adsorption of 2,4-D from water and wastewater. The most widely used method for removing organic compounds is adsorption onto

activated carbon (AC). The large surface area and highly porous structure of AC make it effective for this purpose, even at low concentrations [18]. The high cost of AC has prompted researchers to explore the production of AC from cheaper precursors. Agricultural wastes have been considered an excellent option due to their cost-effectiveness, availability, and dual benefits for both economic and environmental purposes. Marsolla et al [19] studied the adsorption of 2,4-D herbicide using activated carbons. There have been numerous studies on the production of AC from agricultural by-products including bamboo waste [20], rambutan peel [21], pistachio shell [22], water caltrop husk [23], walnut shells [24], apricot stones [25] and olive-waste [26]. Coconut shell granular activated carbon is an excellent adsorbent medium due to its high surface area-to-volume ratio. A large number of contaminant molecules accumulate on this high surface area [27]. The purpose of this study was to determine the adsorption capacity of 2,4-D on coconut shell granular activated carbon (GAC). To investigate the adsorption mechanism of herbicide molecules on the GAC surface, equilibrium data were used to study the adsorption process design. The effects of the initial concentration of 2,4-D, contact time, pH, and adsorbent dosage were examined

1. Theory

1.1 Adsorption isotherm

The equilibrium data were analyzed using the most common isotherms: Langmuir and Freundlich models, which can be explained as follows:

1.1.1 Langmuir isotherm

The Langmuir isotherm specifically describes homogeneous monolayer adsorption onto a surface that contains a finite number of uniform adsorption sites, without transmigration of the adsorbate in the

plane of the surface [28]. The linear form of Langmuir isotherm Equation is given as:

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

C_e (mg/l) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent, q_m (mg/g) is a monolayer adsorption capacity, and b (l/mg) is the equilibrium adsorption constant. The separation factor, R_L [29] describes essential characteristics of Langmuir isotherm as in Equation (2):

$$R_L = \frac{1}{(1+bC_0)} \quad (2)$$

C_0 is the highest initial solute concentration and b is Langmuir's adsorption constant

(l/mg) If:

$R_L > 1$ Unfavorable adsorption

$R_L = 1$ Linear adsorption

$0 < R_L < 1$ Favorable adsorption

$R_L = 0$ Irreversible adsorption

1.1.2 Freundlich isotherm

Freundlich isotherm assumes heterogeneous surface energies, which are derived from Langmuir equations by varying the surface coverage [30]. Freundlich's isotherm can be expressed in its logarithmic form as follows:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (3)$$

C_e is the equilibrium concentration of the adsorbate (mg/l), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), and K_F and n are Freundlich constants, with n indicating how favorable the adsorption process is.

1.1.3 Process design

The objective of the design is to reduce the concentration of C_0 in 2,4-D solution of volume V (L) to C_e (mg/l) in a batch adsorption system that uses a single stage. The required mass of GAC is M (g), and the 2,4-D loading on GAC changes from q_0 to q_e (mg/g) at $t = 0$, $q_0 = 0$ and as equilibrium is approached. The mass balance equates the 2,4-D removed from solution to that adsorbed on GAC as expressed in Equation (4):

$$V(C_0 - C_e) = M(q_e - q_0) = Mq_e \quad (4)$$

Substitution of the Freundlich isotherm equation into Equation (4) and its subsequent manipulation and rearrangement gives Equation (5).

$$M = \frac{VRC_0}{100K_F(C_0(1-\frac{R}{100}))^{1/n}} \quad (5)$$

Equation (5) was used to calculate the mass M (g) of GAC required to achieve any given percent removal (R) from aqueous solution of volume V (L) for any given initial concentration of 2, 4-D C_0 (mg/l), except for 100% removal.

2. Materials and Methods

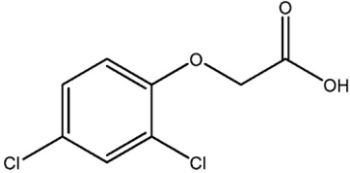
2.1 2,4-Dichlorophenoxyacetic acid

2,4-Dichlorophenoxyacetic acid (2,4-D) of 97% purity obtained from Sigma-Aldrich (M) Sdn. Bhd., UK was used as adsorbate. 2,4-D stock solutions were prepared by accurately weighing the required amount and dissolving it in distilled water using a magnetic stirring method. Using distilled water, various concentrations of 2,4-D solution were prepared as required. The chemical structure and properties of 2,4-D are shown in Table 1.

2.2 Granular activated carbon

Amazon, UK, supplied granular activated carbon (GAC). Activated carbon was produced from coconut shells and used in this research without further processing.

Table 1: Structural properties of the studied herbicide.

Characteristic	2,4-Dichlorophenoxyacetic acid
Pesticide class	Phenoxy herbicide
Chemical structure	
Molecular formula	$C_8H_6Cl_2O_3$
Molecular weight g/mol	221.04
Solubility in water mg/l	900
Melting point: °C	140.5
Boiling point °C	160
Purity, %	95.5
Appearance	White powder, crystal powder
Synonym:	2,4-D

2.3 Characterization of activated carbon

To determine the physical and chemical properties of granular activated carbon, it is important to characterize it. Using the Brunauer-Emmett-Teller (BET) N_2 adsorption method, the specific surface area, total pore volume, average pore diameter, and pore size distribution of the AC were examined. A nitrogen (N_2) adsorption-desorption experiment at 196 °C (77 °K) with a saturation pressure of 106.65 kPa was carried out on GAC. The porosity and surface morphology of GAC were examined using a Scanning Electron Microscope (SEM).

2.4 Batch adsorption procedure

To investigate the effects of contact time, initial 2,4-D concentration, initial solution pH, and activated carbon dosage, on the adsorption uptake of 2,4-D by GAC, batch adsorption equilibrium experiments were conducted. The 2,4-D solution was mixed with 0.5 g GAC in a 200 ml stoppered glass at a temperature of 20 ± 2 °C and agitation speed of 130 rpm for each batch experiment. In each batch experiment, 200 ml of 2,4-D were agitated with 0.5 g GAC at the required initial concentration (10–50 mg/l). In preliminary experiments, the dose of GAC used was found to be optimal for the range of initial 2,4-D concentrations studied. Equilibrium studies were carried out at pH 2-3. Using a dual beam UV/VIS spectrophotometer an absorbance measurement at 283 nm was performed after the desired contact time. Figure 1 shows the calibration curve of 2,4-D absorbance at different initial concentrations. Used Equation (6) and (7), respectively to determine the adsorption capacity after a specific contact time, q_t (mg/g), and the rate of removal, R (%).

$$q_t = \frac{(C_0 - C_t)V}{C_e} \times 100 \quad (6)$$

$$R = \frac{C_0 - C_e}{C_0} \times 100 \quad (7)$$

C_0 (mg/l) liquid phase concentrations of 2,4-D at the initial and time t , respectively, M (g) the dry mass of the GAC used and V (L) the volume of solution treated. The adsorption capacity at equilibrium, q_e (mg/g), was calculated using Equation (8):

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (8)$$

C_e (mg/l) is the equilibrium concentration of 2, 4-D.

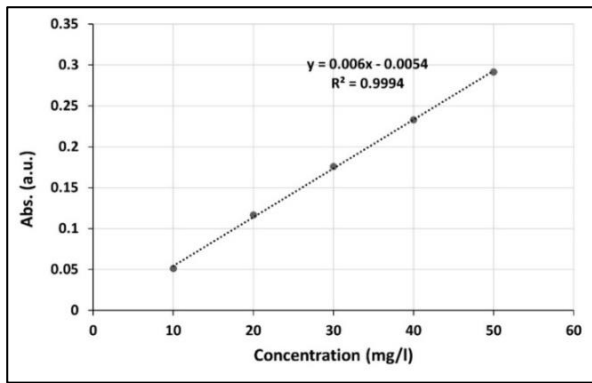


Figure 1: Calibration curve of 2,4-D absorbance at different initial concentrations.

2.4.1 Effect of pH

The effect of solution pH on herbicide removal was examined by changing the solution's pH from 2 to 10. pH was adjusted with 0.1 M HCl and/or 0.1 M NaOH, and pH was measured with a pH meter. The initial 2,4-D concentration was fixed at 50 mg/l, and activated carbon was supplemented with 0.50 g/200 ml at a temperature of 20 ± 2 °C.

2.4.2 Effect of GAC dosage

The effects of GAC dose on 2,4-D adsorption were studied by adding different amounts of GAC (0.2, 0.4, 0.6, 0.8, and 1.00 g) into 200 ml stoppered glasses containing a specified volume (200 ml in each glass) of 2,4-D solution with a fixed initial concentration of 50 mg/l at 20 ± 2 °C, and 130 rpm for 3 hours and measuring the equilibrium concentrations of 2,4-D.

3. Results and Discussion

3.1 Characterization of GAC.

3.1.1 BET

Figure 2 shows the nitrogen adsorption and desorption isotherms for GAC at 77 K, which are classified as type I by the International Union of Pure and Applied Chemistry (IUPAC) [26]. The IUPAC defines adsorbent pores by their pore width as micropores (< 2 nm), mesopores (2–50 nm) and macropores (> 50 nm) [31]. The Brunauer-Emmett-Teller (BET) surface area of GAC obtained is 832.347 m²/g, which is greater than the surface area of conventional commercial AC made from coal. The BET surface areas of the papers by Bahrami *et al.* [32], Alhogbi *et al.* [33], and Lazarotto *et al.* [34] for the removal of 2,4-D from aqueous solutions with commercial granular AC derived from coal-based sources were 600–650, 731.48, and 790 m²/g, respectively. Figure 2 shows the pore size distribution of GAC, which is mostly micropores. Type I isotherms are characterized by simultaneous micropore presence. The relatively high cumulative pore volume of GAC (0.548 cm³/g) is consistent with the high surface area obtained. Figure 3 shows the pore size distribution of the granular activated carbon. The sharpest peak was found between pore diameters of 0 and 1 nm, and the average pore diameter of the prepared sample was 0.899 nm. As a result, the GAC was micropores, with relatively large surface areas and volumes compared to commercially available activated carbons such as Merck's BDH, F100, and Calgon's BPL [35]. A summary of the micropore size, pore volume, and surface area for GAC can be found in Table 2.

Table 2: Physical properties of GAC.

BET surface area (m ² /g)	832.347
Total pore volume of pores (cm ³ /g)	0.548
Micropore volume (cm ³ /g)	0.530
Average pore diameter (Å)	0.899

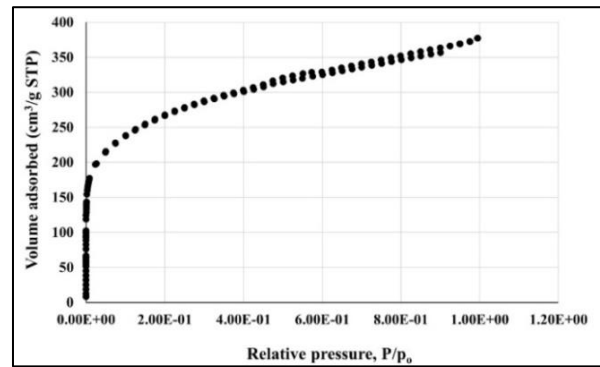


Figure 2: Nitrogen adsorption-desorption isotherms of GAC.

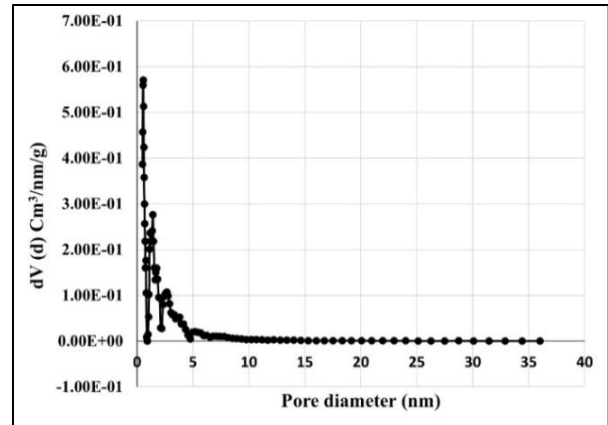


Figure 3: Pore size distribution of GAC.

3.1.2 SEM

The Scanning Electron Microscope (SEM) images of the GAC sample before and after 2,4-D adsorption are depicted in Fig. 4. The surface of the granular activated carbon exhibited large pores indicative of its porous structure. Granular activated carbon is characterized by a substantial surface area and porous structure owing to its well-developed pores. Fig. 4b demonstrates the presence of numerous heterogeneous layers of pores in the GAC, capable of adsorbing 2,4-D molecules. A comparison with the 2,4-D-loaded adsorbent reveals that the surface of the GAC is coated with molecules of 2,4-D.

3.2 Effect of initial 2,4-D concentration and contact time

The effect of a 2,4-D initial concentration range of 10–50 mg/L on 2,4-D adsorption was investigated. To assess the adsorption performance of granular activated carbon (GAC) for 2,4-D at both low and high concentrations, a wide range of 2,4-D concentrations was utilized. It was observed that the equilibrium adsorption capacity increased with an increase in the initial concentration of 2,4-D, reaching 3.76, 6.36, 9.52, 12.24, and 14.48 mg/g, respectively, for initial 2,4-D concentrations of 10, 20, 30, 40, and 50 mg/L at 20 ± 2 °C. This increase in equilibrium adsorption capacity may be attributed to the utilization of all active sites for adsorption at higher 2,4-D concentrations, leading to a larger mass transfer force and more collisions between 2,4-D molecules and GAC. Figure 5 illustrates that the rate of 2,4-D adsorption increased rapidly with time, eventually reaching equilibrium. The contact time required to reach equilibrium was determined to be 3 hours. This figure displays the effect of contact time on 2,4-D removal by granular activated carbon (GAC) across different initial concentrations of 2,4-D at 20 ± 2 °C. Across all initial concentrations of 2,4-D investigated, the adsorption rate escalated with contact time, particularly during the initial stages, before slowing down until equilibrium was achieved after 3 hours. It is possible that the observed faster rate at the beginning is attributed to the larger surface area of GAC available for adsorption for 2,4-D adsorption at the beginning. In the operating conditions, GAC's maximum adsorption capacity is determined by the amount of 2,4-D adsorbed at equilibrium. After the capacity of GAC particles has been exhausted, the rate of removal is then

governed by the rate at which molecules of 2,4-D are transported from the exterior to the interior of the particle. The removal of 2,4-D is contingent upon the concentration of 2,4-D, as depicted in Figure 6; when the initial concentration of 2,4-D is increased, the amount of adsorbed 2,4-D also increases. Specifically, when the initial 2,4-D concentration is elevated from 10 to 50 mg/L, the equilibrium adsorption capacities of GAC rise from 94% to 98.2%. Increasing initial concentrations of 2,4-D enhances its adsorption capacity by providing a driving force to overcome the resistance to mass transfer between the solid and aqueous phases. Consequently, during the adsorption process, the equilibrium may shift, resulting in the removal of more herbicides. A similar pattern has also been observed for methylene blue dye adsorption onto bamboo-based activated carbon [36], cotton waste [37], and adsorption of trichloroethylene from an aqueous solution onto MWCNTs [38].

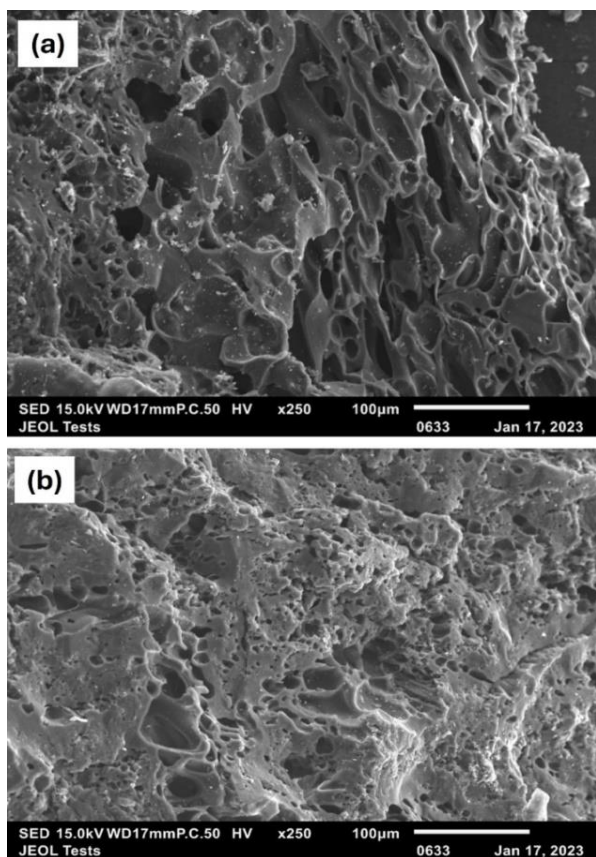


Figure 4: SEM image of GAC x250: a) before and b) after adsorption.

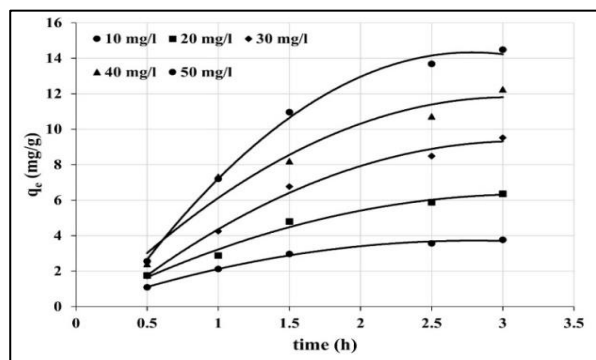


Figure 5: The variation of adsorption uptake with adsorption time at various initial concentrations of 2,4-D (mg/L) onto GAC at 20 ± 2 °C.

3.3 Effect of initial pH

In aqueous solutions, pH stands out as one of the most critical parameters influencing the adsorption process of both the adsorbate and the adsorbent. The pH effect arises from an electrostatic interaction between the adsorbate molecule and the adsorbent surface. Figure 7

demonstrates the impact of pH on the adsorption of 2,4-D by GAC within a pH range of 2 to 10. As the pH of the solution rises, the adsorption capacity of 2,4-D decreases. This phenomenon occurs because, with increasing pH, there is a rise in electrostatic repulsion between the 2,4-D ions and the GAC surface. Consequently, 2,4-D uptake decreases with increasing pH within the studied pH range. Notably, GAC surfaces exhibit positive charges at lower pH levels and negative charges at higher pH levels. Hence, GAC exhibits higher adsorption potential for 2,4-D at lower pH. As Lewis's base, the delocalized electrons in the carbon matrix's basal planes are responsible for GAC's basic properties. A similar trend has also been observed for 2,4-dichlorophenoxyacetic acid sorption onto activated carbon [5].

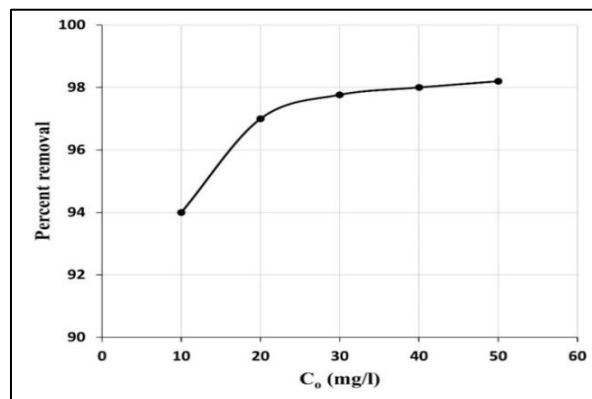


Figure 6: Effect of percent removal at different initial concentrations of 2,4-D at 20 ± 2 °C and 3 h.

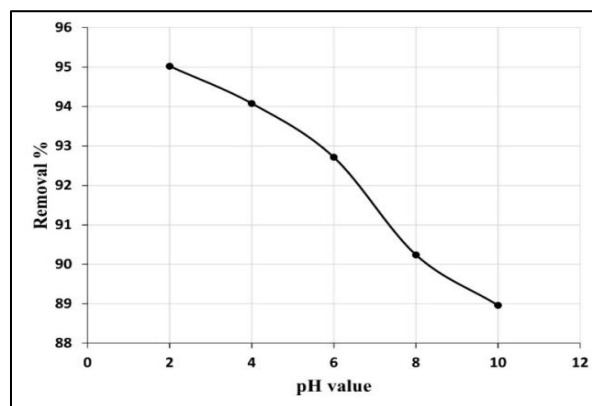


Figure 7: The effect of solution pH on 2,4-D adsorption at 20 ± 2 °C (2, 4-D initial concentration 50 mg/L, agitation speed 120 rpm, GAC dose 0.5 g).

3.4 Effect of GAC dosage

Determining the adsorbent concentration is crucial as it directly influences the adsorbent's capacity at a given initial concentration of 2,4-D. In our experiments, GAC was utilized for adsorption under fixed initial pH (2-3), initial 2,4-D concentration (50 mg/L), and temperature (20 ± 2 °C) for a contact time of 3 hours.

As depicted in Figure 9, the removal of 2,4-D increases with escalating adsorbent dosage, demonstrating a direct dependency on the mass of adsorbent present in the solution. The maximum adsorption efficiency of 2,4-D herbicide onto GAC at 50 mg/L over 3 hours was determined to be 97%. This enhancement in percentage removal can be attributed to the presence of more adsorption sites and an increased adsorption surface area.

Figure 8 further illustrates the impact of adsorbent dosage on the adsorption of 2,4-D onto GAC under conditions of temperature: 20 ± 2 °C and initial concentration: 50 mg/L. Similar behavior was reported for the adsorption of methylene blue on peanut hull [39] and invasive marine seaweed [40].

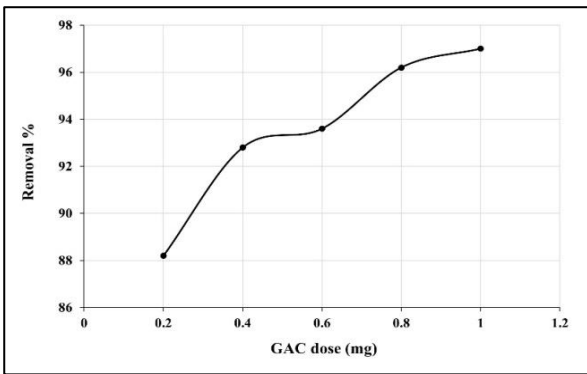


Figure 8: Effect of adsorbent dosage on the adsorption of 2,4-D on GAC ($T = 20 \pm 2 \text{ }^\circ\text{C}$ and $C_0 = 50 \text{ mg/l}$).

3.5 Adsorption isotherms

Adsorption molecules are distributed between the liquid and solid phases when adsorption reaches equilibrium. To find the best model that can be used for designing, the isotherm data should be fitted to different isotherm models [41]. Adsorption isotherms play a critical role in understanding how solutes interact with adsorbents, thereby aiding in optimizing adsorbent utilization. In this study, the adsorption isotherms were examined using two fundamental models: the Langmuir and Freundlich models. These models provide valuable insights into the adsorption behavior of solutes onto adsorbents, guiding the design and optimization of adsorption processes.

3.5.1 Langmuir isotherm

When C_e/q_e was plotted against C_e , a straight line with a slope of $1/q_m$ was obtained, as shown in Figure 9. The correlation coefficient, R^2 value was 0.82, the Langmuir isotherm model was favorable the 2,4-D adsorption data at $20 \pm 2 \text{ }^\circ\text{C}$. The Langmuir constants b and q_m were calculated from Equation (1) and are shown in Table 3. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L). This study found a value of R_L of $0.0.215$ at $20 \pm 2 \text{ }^\circ\text{C}$, confirming that the Langmuir isotherm model was favorable for 2,4-D adsorption onto granular activated carbon.

Table 3: Langmuir and Freundlich isotherm models parameters and correlation coefficients for adsorption of 2,4-D onto GAC.

Model	Parameters	Value
Langmuir	q_m (mg/g)	20.28
	b (l/mg)	0.122
	R^2	0.8157
	R_L	0.215
Freundlich	n	3.25
	K_F	1.998
	R^2	0.955

3.5.2 Freundlich isotherm

Figure 10 shows that the $\log q_e$ versus $\log C_e$ plot indicates a straight line with slope $1/n$ and value 0.31, showing favorable adsorption of 2,4-D on the GAC for the Freundlich isotherm. Accordingly, Freundlich constants K_F and n were calculated from Equation (3) and are listed in Table 4. The Freundlich isotherm model was the best-fit isotherm for the 2,4-D adsorption data, with a correlation coefficient, R^2 of 0.96. Adsorption intensity or surface heterogeneity is measured by the slope of $1/n$ between 0 and 1, becoming more heterogeneous as it approaches zero [41]. When $1/n$ is less than one, Langmuir isotherms are normal, while $1/n$ above one indicates cooperative adsorption [42].

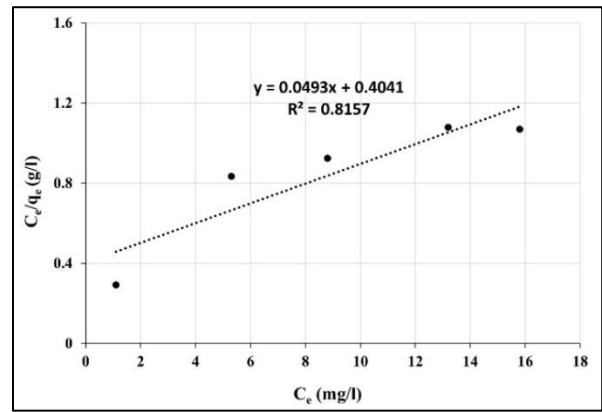


Figure 9: Langmuir isotherm for 2,4-D adsorption at $20 \pm 2 \text{ }^\circ\text{C}$.

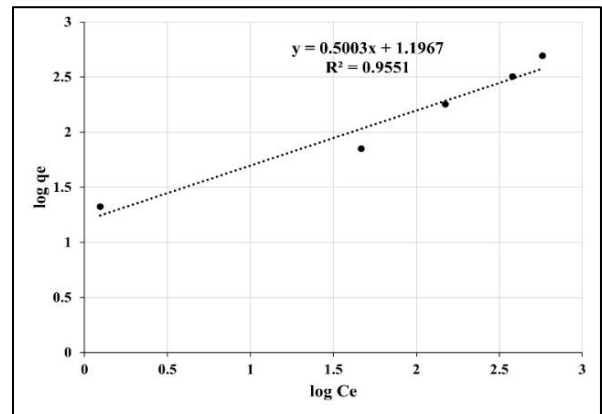


Figure 10: Freundlich isotherm for 2,4-D adsorption at $20 \pm 2 \text{ }^\circ\text{C}$.

5.6 Single-stage batch adsorption process design

Adsorption isotherm data can be used to predict the design of single-batch adsorption systems. Adsorbent quantities can be designed for different solution volumes according to the best-fit isotherm. In Figure 11, the estimated mass of granular activated carbon (GAC) required to remove 2,4-D from a solution at 50 mg/L is shown, with percentage removals of 60%, 70%, 80%, and 90% for different solution volumes (50–100 L). To estimate the mass M (g) of GAC required to remove any given percent 2,4-D from any given volume V (L) of aqueous solution, Equation (5) was applied except for 100% removal. As the volume of the solution to be treated increased, the amount of adsorbent needed also increased. It was found that for the removal of 2,4-D from an aqueous solution with a concentration of 50 mg/l, the required mass of granular activated carbon (GAC) was 31.22, 34.21, 36.94, 39.49, 41.89, and 44.15 grams for solution volumes of 50, 60, 70, 80, 90, and 100 liters, respectively.

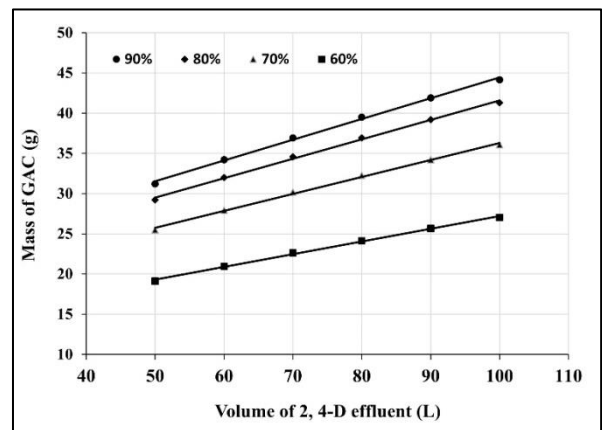


Figure 11: Variation of mass of GAC with volume of 2, 4-D solution treated for various percent removal of 2,4-D of 50 mg/l initial concentration at $20 \pm 2 \text{ }^\circ\text{C}$.

4. Conclusion

According to this study, GAC (Granular Activated Carbon) can be used as an adsorbent for removing 2,4-D from aqueous solutions. The amount of adsorbent, the initial concentration of 2,4-D, and the contact time between 2,4-D and the adsorbent affect the percentage of removal. It was found that GAC could remove 94% to 98.2% of 2,4-D from solutions with initial concentrations between 10 and 50 mg/L within a contact time of 3 hours. An increase in the adsorbent mass, and consequently in the surface area, resulted in a greater amount of 2,4-D adsorbed. The adsorption capacity of 2,4-D on GAC increases as the pH of the solutions decreases. Freundlich adsorption isotherms provided the best correlation for 2,4-D adsorption onto GAC. To remove 2,4-D from wastewater by adsorption onto GAC at a fixed percentage, the amount of adsorbent required can be readily predicted. The study concludes that GAC is an effective adsorbent for the removal of 2,4-D from aqueous wastewater based on these results.

Data Availability

The datasets used and analyzed during the current study are available from the corresponding author upon reasonable request.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgment

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References

- Hazrin, H.M.M.N., Lim, A., Li, C., Chew, J.J., Sunarso, J. (2022) Adsorption of 2, 4-dichlorophenoxyacetic acid onto oil palm trunk-derived activated carbon: Isotherm and kinetic studies at acidic, ambient condition, *Materials Today: Proceedings* **64**: 1557-1562.
- Shankar, M., Anandan, S., Venkatachalam, N., Arabindoo, B., Murugesan, V. (2006) Fine route for an efficient removal of 2, 4-dichlorophenoxyacetic acid (2, 4-D) by zeolite-supported TiO₂, *Chemosphere* **63**: 1014-1021.
- Morton, P.A., Fennell, C., Cassidy, R., Doody, D., Fenton, O., Mellander, P.E., Jordan, P. (2020) A review of the pesticide MCPA in the landâ€œwater environment and emerging research needs, *Wiley Interdisciplinary Reviews: Water* **7**: e1402.
- Alam, J., Dikshit, A.K., Bandyopadhyay, M. (2005) Evaluation of thermodynamic properties of sorption of 2, 4-D and atrazine by tire rubber granules, *Separation and Purification Technology* **42**: 85-90.
- Njoku, V., Hameed, B. (2011) Preparation and characterization of activated carbon from corncob by chemical activation with H₃PO₄ for 2, 4-dichlorophenoxyacetic acid adsorption, *Chemical Engineering Journal* **173**: 391-399.
- Orduz, A.E., 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, *Journal of Environmental Chemical Engineering* **9**: 104601.
- Xi, Y., Mallavarapu, M., Naidu, R. (2010) Adsorption of the herbicide 2, 4-D on organo-palygorskite, *Applied Clay Science* **49**: 255-261.
- Derylo-Marczewska, A., Blachnio, M., Marczewski, A., Swiatkowski, A., Tarasiuk, B. (2010) Adsorption of selected herbicides from aqueous solutions on activated carbon, *Journal of thermal analysis and calorimetry* **101**: 785-794.
- Organization, W.H. (2002) Guidelines for drinking-water quality, ed., World Health Organization.
- Gupta, V.K., Ali, I., Saini, V.K. (2006) Adsorption of 2, 4-D and carbofuran pesticides using fertilizer and steel industry wastes, *Journal of Colloid and Interface Science* **299**: 556-563.
- Vinayagam, R., Pai, S., Murugesan, G., Varadavenkatesan, T., Narayanasamy, S., Selvaraj, R. (2022) Magnetic activated charcoal/Fe₂O₃ nanocomposite for the adsorptive removal of 2, 4-Dichlorophenoxyacetic acid (2, 4-D) from aqueous solutions: synthesis, characterization, optimization, kinetic and isotherm studies, *Chemosphere* **286**: 131938.
- Nabih, M.H., El Hajam, M., Boulika, H., Chiki, Z., Tahar, S.B., Kandri, N.I., Zerouale, A. (2023) Preparation and characterization of activated carbons from cardoon â€œCynara Cardunculusâ€œ waste: Application to the adsorption of synthetic organic dyes, *Materials Today: Proceedings* **72**: 3369-3379.
- Danish, M., Pin, Z., Ziyang, L., Ahmad, T., Majeed, S., Yahya, A.N.A., Khanday, W.A., Khalil, H.A. (2022) Preparation and characterization of banana trunk activated carbon using H₃PO₄ activation: A rotatable central composite design approach, *Materials Chemistry and Physics* **282**: 125989.
- Wazir, A.H., Haq, I.u., Manan, A., Khan, A. (2022) Preparation and characterization of activated carbon from coal by chemical activation with KOH, *International Journal of Coal Preparation and Utilization* **42**: 1477-1488.
- Jung, B.K., Hasan, Z., Jhung, S.H. (2013) Adsorptive removal of 2, 4-dichlorophenoxyacetic acid (2, 4-D) from water with a metalâ€œorganic framework, *Chemical Engineering Journal* **234**: 99-105.
- de Souza, F.M., dos Santos, O.I.A.A. (2022) Assessment of fixed bed adsorption of 2, 4-D herbicide onto modified bentonite clay, *Water, Air, & Soil Pollution* **233**: 158.
- Yang, X., Muhammad, T., Yang, J., Yasen, A., Chen, L. (2020) In-situ kinetic and thermodynamic study of 2, 4-dichlorophenoxyacetic acid adsorption on molecularly imprinted polymer based solid-phase microextraction coatings, *Sensors and Actuators A: Physical* **313**: 112190.
- Ahmad, A.A., Al-Raggad, M., Shareef, N. (2021) Production of activated carbon derived from agricultural by-products via microwave-induced chemical activation: a review, *Carbon Letters* **31**: 957-971.
- Marsolla, L.D., Brito, G.M., Freitas, J.C.C., Coelho, E.R.C. (2022) Removing 2, 4-D micropollutant herbicide using powdered activated carbons: the influence of different aqueous systems on adsorption process, *Journal of Environmental Science and Health, Part B* **57**: 588-596.
- Ahmad, A., Hameed, B. (2010) Fixed-bed adsorption of reactive azo dye onto granular activated carbon prepared from waste, *Journal of Hazardous Materials* **175**: 298-303.
- Njoku, V., Foo, K., Asif, M., Hameed, B. (2014) Preparation of activated carbons from rambutan (*Nephelium lappaceum*) peel by microwave-induced KOH activation for acid yellow 17 dye adsorption, *Chemical Engineering Journal* **250**: 198-204.
- Baytar, O., Åzahin, Å.m., Saka, C., AÅYrak, S. (2018) Characterization of microwave and conventional heating on the pyrolysis of pistachio shells for the adsorption of methylene blue and iodine, *Analytical Letters* **51**: 2205-2220.
- Lin, Y.-Q., Tsai, W.-T. (2021) Liquid-phase removal of methylene blue as organic pollutant by mesoporous activated carbon prepared from water caltrop husk using carbon dioxide activation, *Processes* **9**: 238.
- Lan, D., Chen, M., Liu, Y., Liang, Q., Tu, W., Chen, Y., Liang, J., Qiu, F. (2020) Preparation and characterization of high value-added activated carbon derived from biowaste walnut shell by KOH activation for supercapacitor electrode, *Journal of Materials Science: Materials in Electronics* **31**: 18541-18553.
- Bouchelkia, N., Tahraoui, H., Amrane, A., Belkacemi, H., Bollinger, J.-C., Bouzaza, A., Zoukel, A., Zhang, J., Mouni, L. (2023) Jujube stones based highly efficient activated carbon for methylene blue adsorption: Kinetics and isotherms modeling, thermodynamics and mechanism study, optimization via response surface methodology and machine learning approaches, *Process Safety and Environmental Protection* **170**: 513-535.
- Abdessemed, A., Rasalingam, S., Abdessemed, S., Djebbar, K.E.Z., Koodali, R. (2019) Impregnation of ZnO onto a vegetal activated carbon from algerian olive waste: A sustainable photocatalyst for degradation of ethyl violet dye, *International Journal of Photoenergy* **2019**: 1-13.
- Salman, J., Hameed, B. (2010) Adsorption of 2, 4-dichlorophenoxyacetic acid and carbofuran pesticides onto granular activated carbon, *Desalination* **256**: 129-135.
- Jawad, A.H., Abdulhameed, A.S., Bahrudin, N.N., Hum, N.N.M.F., Surip, S., Syed-Hassan, S.S.A., Yousif, E., Sabar, S. (2021) Microporous activated carbon developed from KOH activated biomass waste: surface mechanistic study of methylene blue dye adsorption, *Water Science and Technology* **84**: 1858-1872.
- Hameed, B., Ahmad, A., Aziz, N. (2009) Adsorption of reactive dye on palm-oil industry waste: equilibrium, kinetic and thermodynamic studies, *Desalination* **247**: 551-560.
- Ahmad, A., Hameed, B. (2009) Reduction of COD and color of dyeing effluent from a cotton textile mill by adsorption onto bamboo-based activated carbon, *Journal of hazardous materials* **172**: 1538-1543.
- Everett, D.H. (1972) Manual of symbols and terminology for physicochemical quantities and units, appendix II: Definitions, terminology and symbols in colloid and surface chemistry, *Pure and Applied Chemistry* **31**: 577-638.
- Bahrami, M., Amiri, M.J., Beigzadeh, B. (2018) Adsorption of 2, 4-dichlorophenoxyacetic acid using rice husk biochar, granular activated carbon, and multi-walled carbon nanotubes in a fixed bed column system, *Water Science and Technology* **78**: 1812-1821.
- Alhogbi, B.G., Altayeb, S., Bahaidarah, E.A., Zawrah, M.F. (2021) Removal of anionic and cationic dyes from wastewater using activated carbon from palm tree fiber waste, *Processes* **9**: 416.
- Lazarotto, J.S., da Boit Martinello, K.t., Georgin, J., Franco, D.S., Netto, M.S., Picilli, D.G., Silva, L.F., Lima, E.C., Dotto, G.L. (2021) Preparation of activated carbon from the residues of the mushroom (*Agaricus bisporus*) production chain for the adsorption of the 2, 4-dichlorophenoxyacetic herbicide, *Journal of Environmental Chemical Engineering* **9**: 106843.
- Tan, I., Ahmad, A., Hameed, B. (2008) Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk:

- Equilibrium, kinetic and thermodynamic studies, *Journal of Hazardous Materials* **154**: 337-346.
- [36] Hameed, B., Din, A.M., Ahmad, A. (2007) Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies, *Journal of Hazardous Materials* **141**: 819-825.
- [37] Ertay, M., Acemiolu, B., Alma, M.H., Usta, M. (2010) Removal of methylene blue from aqueous solution using cotton stalk, cotton waste and cotton dust, *Journal of Hazardous Materials* **183**: 421-427.
- [38] Liang, J., Liu, J., Yuan, X., Dong, H., Zeng, G., Wu, H., Wang, H., Liu, J., Hua, S., Zhang, S. (2015) Facile synthesis of alumina-decorated multi-walled carbon nanotubes for simultaneous adsorption of cadmium ion and trichloroethylene, *Chemical Engineering Journal* **273**: 101-110.
- [39] Gong, R., Li, M., Yang, C., Sun, Y., Chen, J. (2005) Removal of cationic dyes from aqueous solution by adsorption on peanut hull, *Journal of Hazardous Materials* **121**: 247-250.
- [40] Cengiz, S., Cavas, L. (2008) Removal of methylene blue by invasive marine seaweed: *Caulerpa racemosa* var. *cylindracea*, *Bioresource Technology* **99**: 2357-2363.
- [41] Hameed, B., Ahmad, A. (2009) Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass, *Journal of Hazardous Materials* **164**: 870-875.
- [42] Tan, I., Hameed, B., Ahmad, A. (2007) Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon, *Chemical Engineering Journal* **127**: 111-119.