FACULTY OF SCIENCE AND EDUCATION

DEPARTMENT OF CHEMISTRY

ADSORPTION AND KINETICS OF CHLORPYRIFOS FROM WASTEWATER USING ACTIVATED CARBON FROM ORANGE PEELS:

BY

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ARESEARCH PROJECT REPORT SUBMITTED TO THE DEPARTMENT OF CHEMISTRY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF A BACHELOR'S DEGREE IN SCIENCE AND EDUCATION OF BUSITEMA UNIVERSITY

AUGUST, 2026.

DECLARATION

I, Adiyo Nancy, declare that this research project is my original work and has not been submitted to any other institution for academic credit.

Signature: ……  **……**

Date: …… 28th/08/2026 **.**

APPROVAL

This research project has been submitted with the approval of the supervisor.

Supervisor's Name: DR. KIGOZI MOSES .....

Signature: ....

Date: 29/08/2026 .....

DEDICATION

I dedicate this research report to Almighty God, the source of my strength, wisdom and perseverance. To my aunties Hellen Kalongo and Aboda Tarcisia whose unconditional love, prayers and endless sacrifices made my education possible and to my supervisor Dr. Kigozi Moses for the encouragement, guidance and support right from writing proposal until the finishing point.

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ABSTRACT

Widespread agricultural use of Chlorpyrifos leads to severe surface runoff and aquatic contamination. Traditional wastewater treatments fail to eliminate this persistent, lipophilic pollutant, posing human health risks like neurotoxicity. Commercial activated carbon effectively captures such organic pollutants but remains prohibitively expensive. Utilizing abundant agricultural waste like orange peels offers a dual solution for cost-effective environmental remediation and sustainable waste management. The study aimed to synthesize and characterize orange peel-derived activated carbon (OPAC), evaluate optimal operating parameters (pH, dosage, contact time), and examine adsorption kinetics and isotherms. Prepared orange peels were chemically activated with phosphoric acid (H_3PO_4) at a 1:2 w/w ratio and carbonized. Characterization included Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and iodine number determination. Batch experiments were monitored using UV-Vis spectrophotometry at a maximum wavelength of 290 nm to trace Chlorpyrifos concentrations. Characterization confirmed a highly active material with a prominent iodine number of 435.0. pH optimization revealed that Chlorpyrifos removal is significantly higher in acidic mediums, peaking at an 87.5% removal efficiency at pH 3.0 and decreasing sharply past the point of zero charge (pH_{zpc}=7.0). Kinetic data aligned closely with the pseudo-second-order model (R^2=0.9954), showing a calculated equilibrium capacity (q_e) of 7.07 mg/g and establishing that chemisorption is the rate-limiting step. Equilibrium profiling demonstrated an excellent fit with the Langmuir isotherm model (R^2 = 0.9944), yielding a maximum monolayer capacity (Q_m) of 10.57 mg/g and a favorable dimensionless separation factor (R_L) of 0.3339. Conversely, the Freundlich model was unfavorable (n = 1.8202). In conclusion, orange peel-derived activated carbon serves as a highly efficient, ecologically sustainable, and low-cost bio-adsorbent for remediating pesticide-polluted water systems.

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LIST OF ABBREVIATIONS

CPYO: Chlorpyrifos-Oxon

TCP: 3, 5, 6-trichloro-2-pyridinol

SEM: Scanning Electron Microscopy

UV-Vis: Ultraviolet-Visible

OPAC: Orange Peel Activated Carbon

FTIR: Fourier Transform Infrared.

EDX; Energy Dispersive X-ray

CHAPTER ONE: INTRODUCTION

1.1: Background of the Study.

Chlorpyrifos is an organophosphate insecticide extensively used in agricultural practices worldwide, including in Uganda. Its widespread application has led to concerns regarding water pollution, posing significant risks to aquatic ecosystems and human health due to its inherent toxicity and resistance in the environment (Joshi V J. M., 2023). Traditional wastewater treatment methods often prove insufficient to effectively remove such persistent organic pollutants. Hence, there is a pressing need for the development of cost-effective, efficient and environmentally sustainable methods for detoxifying Chlorpyrifos-contaminated water sources (Joshi V J. M., 2023).

Adsorption has been recognised as one of the most promising physical processes for pesticide removal due to its efficiency and relative ease of implementation. Activated carbon, known for its high surface area and porous structure, is a highly effective adsorbent for a wide range of pollutants. However, commercial activated carbon can be expensive (Kainth S, 2024). The utilisation of agricultural waste, such as orange peels, for the production of activated carbon offers a sustainable and economically viable option. Orange peels are abundant biomass waste, and their conversion into activated carbon presents a double benefit: effective waste management and the creation of an efficient adsorbent. Studies have demonstrated that activated carbon derived from orange peels can have a significantly higher sorption capacity compared to natural dried orange peels (Ettish M, 2021).

Chlorpyrifos is practically insoluble in water and its solubility in pure water is approximately 1.39 mg/L at 25^{O}C. Other established literature values tell us it may be as low as 0.73 mg/L at the same temperature. This low solubility indicates that Chlorpyrifos does not readily dissolve in aquatic environments and tends to remain in solid or adsorbed states. In contrast to its behavior in water, Chlorpyrifos is highly soluble in many organic solvents thus highlighting its lipophilic nature with Benzene at 790 g/L, Acetone at 650 g/L, Chloroform at 630 g/L, Diethyl ether at 510 g/L and Methanol at 45 g/L (Joshi V J. M., 2023).

Chlorpyrifos enters aquatic systems and wastewater through several distinct routes primarily originating from its use in agricultural fields. The most significant pathway to water bodies is through surface runoff and soil erosion during rainfall or irrigation because Chlorpyrifos strongly adsorbs to soil particles, it often migrates to water bodies as soil-bound contaminants rather than in a purely dissolved state. During application, a portion of the pesticide can go directly into nearby water sources through atmospheric spray drift. While its high soil-sorption capacity limits some movement, Chlorpyrifos can still leach into groundwater through irrigation and rainfall drainage. Chlorpyrifos and its metabolites can travel many kilometers through the atmosphere before depositing into soil or water far from the original application site (Ettish M, 2021).

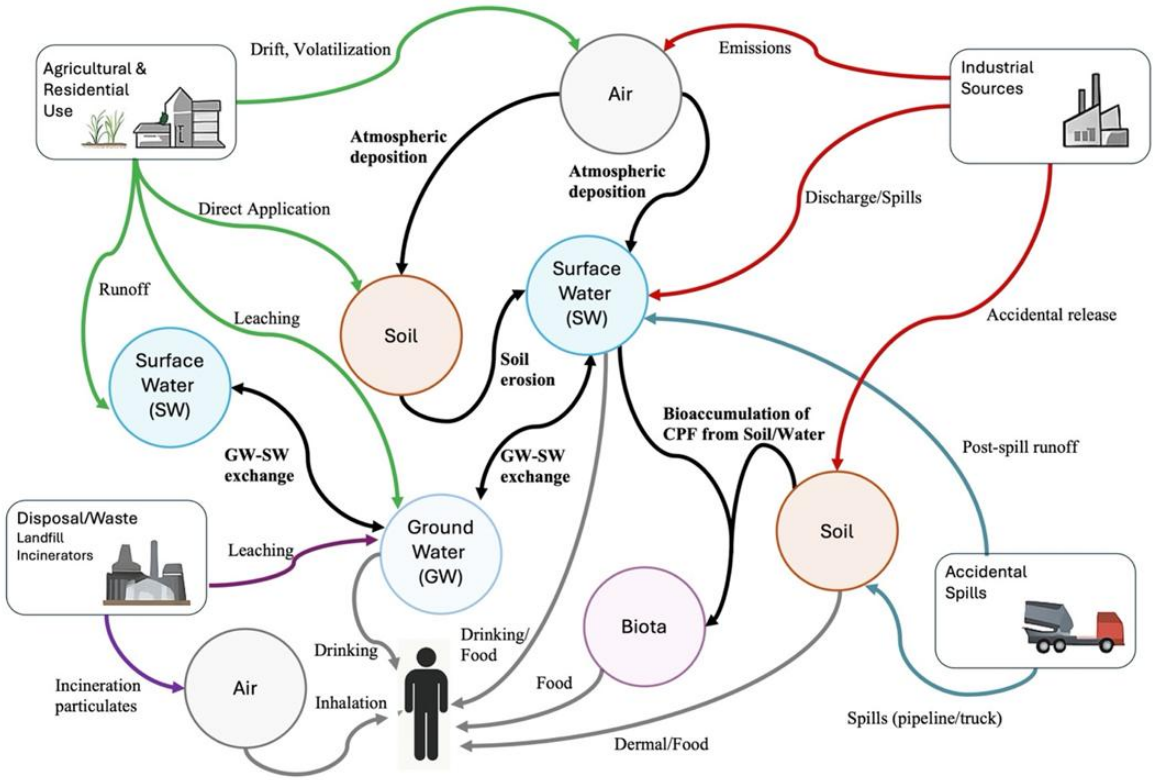


Figure 1. Pathways of chlorpyrifos entry into aquatic environments

Figure 1: pathways of chlorpyrifos entry into aquatic environments

Once in the environment, Chlorpyrifos undergoes several degradation processes that change its chemical structure and toxicity. The primary degradation pathway in both water and soil is hydrolyzed which breaks Chlorpyrifos down into its major metabolite, 3, 5, 6-trichloro-2-pyridinol. This process can be abiotic or biotic with abiotic hydrolysis occurring faster at higher pH levels. In the air or on plant surfaces,

Chlorpyrifos can undergo photolysis and oxidation to form chlorpyrifos-Oxon CPYO is significantly more toxic than the parent compound, though it often degrades quickly into TCP. TCP itself is broken down by specific microorganisms or through chemical processes into secondary metabolites like 2-hydroxypyridine and 6-chloro-2-pyridinol, eventually mineralizing into small molecular compounds and carbon oxides (Ettish M, 2021).

1.2: Problem statement.

Chlorpyrifos is a widely used organophosphate insecticide that has become a significant environmental concern due to its toxicity, persistence and tendency to bioaccumulate in aquatic ecosystems. Efficient conventional wastewater treatment methods often fail to eliminate this recalcitrant pollutant, allowing it to contaminate groundwater and surface water, posing a severe risk to human health, including neurotoxicity and endocrine disruption. While commercial activated carbon is effective at removing such pollutants, its high cost limits its application in many regions. Simultaneously, the agricultural industry generates large quantities of waste, such as orange peels, which are often improperly disposed of, causing further environmental degradation. Although previous studies have explored agricultural waste-derived adsorbents, there remains a need to optimise the production, characterisation, and adsorption kinetics of orange peel-based activated carbon specifically for Chlorpyrifos removal to ensure high efficiency and economic viability. Therefore, this study addresses the environmental and economic problem of removing toxic Chlorpyrifos from wastewater by developing a low-cost, sustainable and eco-friendly activated carbon from orange peels.

1.3: Objectives

1.3.1: General Objective

To develop a sustainable, environmentally friendly and inexpensive adsorbent from orange peels to remediate wastewater polluted with Chlorpyrifos.

1.3.2: Specific Objectives

i. To prepare and characterise activated carbon from orange peels and assess its physicochemical properties.

ii. To determine the optimal operational parameters pH, adsorbent dosage, contact time, initial concentration for Chlorpyrifos adsorption from aqueous solutions as well as evaluate the maximum adsorption capacity of the prepared activated carbon for Chlorpyrifos using various isotherm models.

iii. To study the adsorption kinetics of Chlorpyrifos onto the activated carbon from orange peels, identifying the rate-limiting steps and fitting experimental data to appropriate kinetic models.

1.4: Research Questions

1. Can activated carbon derived from orange peels effectively adsorb Chlorpyrifos from aqueous solutions?
2. What are the optimal conditions (pH, adsorbent dosage, contact time, initial Chlorpyrifos concentration) for the adsorption of Chlorpyrifos by activated carbon from orange peels?
3. What is the adsorption capacity of activated carbon from orange peels for Chlorpyrifos?
4. What kinetic models best describe the adsorption process of Chlorpyrifos onto activated carbon from orange peels?

1.5: Justification

Chlorpyrifos is a widely used organophosphate insecticide that poses significant environmental and health risks due to its resistance, toxicity, and global distribution. Its presence in wastewater, particularly from agricultural runoff contaminates water bodies and can lead to neurological damage in both humans and animals. The metabolites of Chlorpyrifos are often more water-soluble and can contaminate groundwater. This study proposes an innovative, sustainable method for removing Chlorpyrifos from wastewater using activated carbon derived from orange peels and investigates its adsorption efficiency and kinetic. Conventional wastewater treatment methods are often insufficient for removing this recalcitrant pollutant. Current municipal wastewater treatment plants often struggle to remove pesticides adequately, with concentrations sometimes exceeding toxicity benchmarks. Furthermore, the utilization of agricultural waste, such as orange peels, transforms a disposal problem into a valuable resource, promotes a circular economy and reduces waste accumulation.

This study contributes to the advance understanding of adsorption processes and sustainable adsorbent development, investigates physiochemical properties of orange peel-derived activated carbon, explores adsorption kinetics and isotherms and contributes to green chemistry by valorizing waste into functional materials...

This research directly supports Environmental Regulations Policies like the EU Water Framework Directive, provides a potential low-cost and efficient solution for industries and municipalities to meet stringent environmental standards and promotes Sustainable Waste Management and green technologies.

This study is directly relevant to several United Nations Sustainable Development Goals. Good Health and Well-being by removing a toxic pesticide like Chlorpyrifos from wastewater, hence reducing health risks associated with contaminated water, Clean Water and Sanitation, the core objective of this research is to enhance wastewater treatment processes, Industry, Innovation, and Infrastructure. The development of a novel, efficient and sustainable wastewater treatment technology using agricultural waste represents innovation in infrastructure. Responsible Consumption and Production by converting agricultural waste (orange peels) into a useful product (activated carbon) for environmental remediation.

1.6: Significance

This research carries significant implications for environmental protection and the promotion of sustainable development in agricultural regions. By valorizing an agricultural waste product orange peel, it proposes a cost-effective and environmentally benign solution to mitigate Chlorpyrifos pollution in water bodies. The findings will enrich the scientific understanding of adsorption mechanisms and kinetics of pesticides on biomass-derived adsorbents, specifically focusing on orange peel-derived materials. Furthermore, this study will generate valuable empirical data essential for the potential design and implementation of small-scale wastewater treatment facilities, thereby offering a tangible solution to address pervasive water contamination issues in agricultural areas around Nagongera-Tororo and similar contexts. The successful outcome of this research could provide a pathway for local communities to address pesticide pollution using readily available resources, enhancing public health and ecological integrity.

1.7: Scope

The scope of this research is meticulously defined to provide a focused and comprehensive investigation into the removal of chlorpyrifos from wastewater using activated carbon produced from orange peels. Synthesis of activated carbon from orange peels through a defined activation process for example chemical or physical activation. Comprehensive characterization of the synthesized activated carbon using techniques such as Fourier transform infrared spectroscopy for functional groups and iodine number for surface area and porosity. Batch Adsorption Experiments to investigate key parameters influencing chlorpyrifos adsorption including effect of Initial Chlorpyrifos Concentration, effect of Adsorbent Dosage, effect of Contact Time and effect of pH. Adsorption Kinetics models which include pseudo-first-order and pseudo-second-order to elucidate the rate-limiting steps and mechanisms of adsorption. Adsorption Isotherms which involve fitting experimental data to isotherm models for example Langmuir and Freundlich models to describe the equilibrium relationship between the adsorbate and adsorbent, providing insights into the adsorption capacity and surface homogeneity. This study will primarily focus on batch adsorption experiments and will not extend to continuous flow systems or regeneration studies unless specified as future work.

1.8: Conceptual Framework

The conceptual framework for this research is built upon the principles of adsorption science, environmental chemistry, and sustainable resource management. Chlorpyrifos contamination in wastewater poses a significant threat to environmental and human health due to its toxicity and persistence. Conventional treatment methods are often insufficient. Adsorption using activated carbon derived from orange peels. The process where adsorbate molecules, chlorpyrifos adhere to the surface of an adsorbent orange peel activated carbon. This occurs due to various forces including Van der Waals forces, electrostatic interactions, hydrogen bonding, and interactions. Orange peel activated carbon is a highly porous material with a large surface area and a variety of surface functional groups (for example hydroxyl, carboxyl, lactone, phenolic groups), which are crucial for efficient adsorption. The porosity and surface chemistry can be optimized through the activation process. Orange peels, being rich in carbonaceous material, serve

as an excellent precursor for activated carbon. These models describe the rate at which chlorpyrifos molecules are adsorbed onto the activated carbon surface. Understanding the kinetics helps determine the time required to reach equilibrium and the rate-limiting step of the adsorption process. These models explain the distribution of chlorpyrifos molecules between the liquid phase and the solid phase at equilibrium, providing information about the maximum adsorption capacity and the nature of the adsorption sites on the adsorbent surface. The utilization of agricultural waste (orange peels) to create a valuable product for environmental remediation embodies the principles of green chemistry and contributes to a circular economy model by transforming waste into a resource.

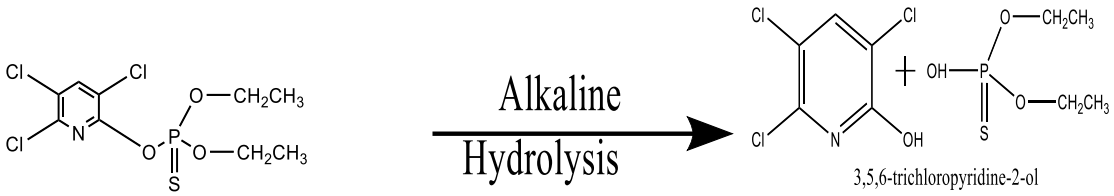
CHAPTER TWO: LITERATURE REVIEW

2.1: Introduction

Chlorpyrifos (O, O-diethyl O-(3, 5, 6-trichloro-2-pyridinyl)-phosphorothioate) is one of the most extensively used organophosphorus insecticides globally, employed in agricultural, domestic, and industrial settings for pest control. Despite their effectiveness, only approximately 0.1% of applied pesticides reach target pests, with the remaining 99.9% entering the environment, contributing to widespread ecological contamination. The contamination of aquatic environments by organophosphorus pesticides has become a global concern due to their high toxicity and persistence. Among these, chlorpyrifos is one of the most widely utilized insecticides in agriculture for pest control. Its presence in wastewater, primarily through agricultural runoff and industrial discharge, poses severe threats to human health and ecological systems. Consequently, the development of efficient, low-cost, and sustainable removal technologies is a priority for environmental chemistry. Adsorption using activated carbon derived from agricultural waste specifically orange peels is a promising technique that aligns with the principles of green chemistry and waste valorization.

2. 2: Chlorpyrifos Environmental Fate and Toxicity

Chlorpyrifos (O, O-diethyl -O-3, 5, 6-trichloro-2-pyridyl phosphorothioate) is characterized by its lipophilic nature and low water solubility. It is widely used for crop protection but often ends up in water bodies where it can persist for extended periods (Hafiz U.R, (2021)). Chlorpyrifos is a potent acetylcholinesterase inhibitor, leading to acute neurotoxicity in both humans and non-target aquatic organisms (Hafiz U.R, (2021)). Chronic exposure is linked to developmental delays, neurological damage, and endocrine disruption. CPF exhibits moderate water solubility (2.0 mg/L at 25°C) and a high octanol-water partition coefficient (log Kow = 4.7–5.11), indicating strong hydrophobicity and tendency to partition into organic phases. Its environmental persistence is notable, with half-life of 35–78 days in water and 60–120 days in soil. In water, chlorpyrifos undergoes degradation into products like 3, 5, 6-trichloro-2-pyridinol, which is more water-soluble and can further contaminate groundwater (Ma J, 2023).



O,O-diethyl-O-3,5,6-trichloropyridine 2-yl phosphorothioate(Chlorpyrifos)

Schematic 1:Breakdown of chlorpyrifos in aquatic environment

Environmental monitoring studies have detected CPF across diverse water bodies at varying concentrations. CPF concentrations of 542.0 mg/L and 396.0 mg/L in river and wastewater in Portugal, respectively. 23.7 mg/L in China's Dongjiang River headwaters, and 2,434.0 mg/L in Greece's Strymonas River basin. Significantly higher concentrations have been documented in industrial effluents with 24.7 mg/L from an agrochemical facility in South Korea, 200 mg/L in Egyptian pesticide industry wastewater, and 805 mg/L from a Malaysian production facility (Ma J, 2023).

2.3: Activated Carbon from Agricultural Waste

The use of agricultural residues as precursors for activated carbon is a sustainable alternative to commercial coal-based carbons. As a major byproduct of the juice industry, orange peels are rich in cellulose, hemicellulose, and pectin. Studies have shown that orange peels can be converted into highly porous activated carbon through chemical or physical activation. Utilizing orange peels reduces waste disposal costs and environmental burdens associated with landfilling. Research indicates that agricultural waste-based AC offers comparable, and sometimes superior, adsorption capacities to commercial variants due to its unique surface functional groups (Denga R.M, 2022).

4: Preparation and Characterization of Orange Peel-Derived Activated Carbon.

The synthesis of activated carbon from orange peels typically involves two stages: carbonization and activation. Chemical activation using agents like phosphoric acid is common for developing high surface area and porosity. SEM reveals an irregular, cavity-filled exterior surface which is essential for trapping chlorpyrifos molecules, identifies functional groups such as hydroxyl (-OH), carboxyl (-COOH), and aromatic C=C bonds that facilitate adsorption through chemical interactions. Iodine number used

to measure specific surface area and pore volume, which are critical predictors of adsorption efficiency (Ettish M, 2021).

2.5: Adsorption

2.5.1: UV-Vis Spectrophotometry in Determination of chlorpyrifos Concentrations.

UV –Vis spectroscopy is an analytical technique that measures the number of discrete wavelengths of UV or Visible light that are absorbed or transmitted through a sample in comparison to a blank sample. The method uses light described by the different wavelengths to analyze and identify different substances by locating the specific wavelengths corresponding to the maximum absorbance. The machine employed in this technique is the UV/Vis spectrometer which may be a single beam or double beam spectrometer. The spectrometer consists of five major components which include; the light source, wave length selector, sample, detector and computer to process output (T, 2023).

The most commonly used light sources in the technique is the tungsten lamps for visible light and deuterium lamp for UV light. The choice of wave length selector will always depend on the sample, type and analyte. The most commonly used wave length selectors are the monochromators which are usually fitted with filters to narrow their wavelength selection and also improve on the signal to noise ratio (T, 2023).

Chlorpyrifos has a strong absorption band centered at (λ_{max}) 229-230nm. The peak absorption of chlorpyrifos using OPAC is (λ_{max}) 230nm. An appropriate light source and wave length selector is chosen and the light passes to the sample placed in a cuvette. For this case distilled water will be used as a blank sample and then chlorpyrifos is the analyte of interest. It is advisable to use quartz cuvettes because quartz is transparent to most of the UV light. Plastics are discouraged for examination because plastic generally absorbs UV light. Light having passed through the sample; the detector converts the light into a readable signal.

The UV – Vis spectroscopy information may be represented as a graph of absorbance, optical density or transmittance as a function of wave length. The wave length is always on the x – axis and the former on the y – axis. The graph is typically referred to as a spectrum. The absorbance (A) is equal to the logarithm of the fraction of light intensity

before passing through the sample (I_o) divided by light after passing through the sample (I). The fraction I divided by I_o is called transmittance (T), which expresses how much light passed in the sample.

The concentration of an analyte in solution can be determined by measuring the absorbance at some wavelength and applying the Lambert– Beer Law (T, 2023).

$$A = \varepsilon\, lc = \log\left(\frac{I_o}{I}\right) = log\left(\frac{I}{T}\right) = -log(T)$$ **…..Eqn (1)**

Where; A-Absorbance, ε-Asorptivity coefficient, l-path length, c-concentration and T-transmittent

2.5.2: Mechanism of Adsorption of chlorpyrifos on orange peels.

The adsorption of chlorpyrifos onto orange peel is governed by physical or chemical processes. In the physical adsorption mechanism, the forces of attraction existing between the adsorbate and the adsorbent are weak van der Waals forces, and the chlorpyrifos molecules attach onto the adsorbent surface under the influence of van der Waals forces. The orange peels provide a porous surface with functional groups that can attract and bind chlorpyrifos molecules through interactions such as electrostatic forces, hydrogen bonding and Van der Waals force. Chlorpyrifos molecules carry a positive charge and the orange peel surface has regions with opposite charge which lead to electrostatic interactions. In the chemical adsorption mechanism, the forces of attraction existing between adsorbate particles and adsorbent are almost of the same strength as chemical bonds, the functional groups on the orange peel surface such as hydroxyl, carboxyl, and other oxygen-containing groups form bonds with the chlorpyrifos molecules (S, 2025).

2.6: Adsorption Isotherms

2.6.1: Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm is used to describe the equilibrium between adsorbate and adsorbent system. The adsorbate adsorption is limited to one molecular layer at or before a relative pressure of unity is reached. It is assumed that the adsorption sites have equal affinities for molecules of adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. The

Langmuir isotherms are useful for determining the efficiency of the adsorbent at higher temperatures. It quantitatively explains the formation of a monolayer adsorbate on the outer surface of the adsorbent, after which no further adsorption takes place. The theoretical Langmuir isotherm is valid for the adsorption of a solute from a liquid solution as a monolayer on a surface containing a large number of identical sites. The linear form of Langmuir equation is as follows;

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m} \text{.....Eqn (2)}$$

Where; q_e is the amount of adsorbate absorbed per unit, q_m is the maximum adsorption capacity for monolayer adsorption, c_e is the equilibrium adsorbate concentration in solution and K_L is Langmuir constant.

The graph of $\frac{1}{q_e}$ against $\frac{1}{C_e}$ gives a straight line where the vertical intercept = $\frac{1}{q_m}$ and slope = $\frac{1}{K_L q_m}$ from which constants; K_L and q_m can be calculated (Xing X, 2022).

2.6.2: Freundlich Adsorption Isotherm

The Freundlich isotherms are applicable only at lower temperatures to provide insight into adsorption phenomena and monolayer coverage on the adsorbent. It is essentially empirical but often useful as a means of data description. The equation generally agrees with the Langmuir equation and experimental data over a moderate concentration range. It is also commonly used to describe the adsorption characteristics of the heterogeneous surface. Freundlich isotherm assumes unlimited sorption sites, which is correlated with a better heterogeneous surface of the adsorbent media. The linear form of Freundlich equation is as follows;

$$\log q_e = \log K_f + \frac{1}{n(\log C_e)} \text{.....Eqn (3)}$$

Where; K_f is the Freundlich adsorption capacity and n is the adsorption intensity, q_e is the amount of adsorbate adsorbed per unit weight of adsorbent and C_e is the equilibrium adsorbate concentration in solution (Xing X, 2022).

A plot of log q_e versus log C_e gives a linear graph with slope = $\frac{1}{n}$ and vertical =logK_f.

2.7 Kinetic Models

Kinetic models are used to test experimental data so as to examine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction. Several kinetic models have been proposed to describe the mechanism by which chlorpyrifos is adsorbed onto adsorbent surfaces. To analyze the adsorption kinetics of chlorpyrifos onto the hydrothermally activated orange peelings (AOP), the pseudo-first-order and pseudo-second-order kinetic models are used to process the data.

2.7.1: Pseudo First Order Model

The pseudo-first order rate model is used as a rate equation for assigning the rate of adsorption of an adsorbate into adsorbent. The linear form of the pseudo-first-order kinetic model is represented by the equation;

$$\frac{dqt}{dt} = K_1(q_o - q_t)$$

And the integrated pseudo first order rate equation is;

$$log(q_o - q_t) = \log q_e - \frac{K_1}{2.303} t \text{.....Eqn (4)}$$

A linear graph of log $(q_e - q_t)$ against time, t must be obtained for the data to fit the pseudo-first order rate mode.

2.7.2: Pseudo Second Order Model

The kinetic rate equation for the pseudo-second order adsorption reaction is expressed as;

$$\frac{dqt}{dt} = K_2(q_o - q_t)^2$$

And the integrated pseudo second order rate equation is;

$$\frac{1}{q_o - q_t} = \frac{1}{q_o} + K_2 t$$

Pseudo-second order kinetic expression for describing the adsorption of some ions onto the adsorbent is also useful for determining q_o and K_2 values from the graph of $\frac{t}{qt}$ against t after rearrangement of the above equation as;

$$\frac{t}{qt} = \frac{1}{K_2 {q_o}^2} + \frac{t}{q_o} \text{ .....Eqn (5)}$$

A linear graph of $\frac{t}{qt}$ against time, t must be obtained for the data to fit the pseudo-second order rate model. The slope of the graph = $\frac{1}{q_o}$ and the vertical intercept = $\frac{1}{K_2 {q_o}^2}$ hence q_o and K_2 values can be determined from the graph Where q_O and q_t in mg/g are the amounts of adsorbed Chlorpyrifos at equilibrium and at any time t, respectively, K_1 and K_2 are equilibrium rate constants of pseudo first and second order reactions (Y, 2006)

CHAPTER THREE: METHODOLOGY

3.1: Materials and reagents

Fresh orange peels, distilled water, phosphoric acid, sodium hydroxide, analytical standard of Chlorpyrifos, acetone, analytical balance (precision 0.0002g), grinder, sieve, drying oven, shaker, pH meter, UV-Visible spectrophotometer, centrifuge, filter paper, conical flasks, volumetric flasks, beakers, measuring cylinders, a stirrer, Burette, stoppers, Beakers, Funnels, Pipette, gloves, lab coat, goggles, marker labels, Hydrochloric Acid (5%), Sodium Thiosulfate, Iodine, Potassium Iodide, Potassium Iodate, Starch, Sodium Carbonate, FTIR, SEM.

3.2: Collection and Preparation of Orange Peels

Fresh oranges were collected from a local fruit vendor. The peels were removed, thoroughly washed with tap water, and then multiple times with distilled water to eliminate dirt, dust and soluble impurities. After washing, the orange peel was cut into small segments to make it easier for drying. Then exposed to sunlight for 3 days before being additionally oven dried for additional 24hrs at 80^oC to achieve a constant weight and to avoid any moisture content. The dried peels were crushed and passed through a sieve to obtain a uniform particle size. The finish goods were stored in clean, airtight polyethylene container.

3.3: Chemical Activation and carbonization.

The prepared powdered orange peel particles were impregnated with phosphoric acid (H_3PO_4) at a specific impregnation ratio of 1:2w/w. The mixture was stirred, then allowed to stand for 24 hours at room temperature to ensure proper impregnation. The impregnated mixture was carbonized by putting in a metallic tin and then placed in a dug hole, fire was set and the sample was allowed to burn for 24 hrs. The resulting activated carbon was removed and cooled, then thoroughly washed with distilled water until the filtrate reached a neutral pH (pH 6.5-7) to remove residual activating agents and impurities. The washed carbon was then oven-dried at 105 °C for three hours. The final activated carbon was stored in airtight containers in a desiccator to prevent moisture absorption prior to characterization and adsorption experiments.

3.4: Characterization of Activated Carbon

3.4.1: physical properties.

The prepared activated carbon was characterized using various advanced techniques to understand its physical and chemical properties; Scanning Electron Microscopy was used to observe the surface morphology, texture and porosity of the adsorbent. Energy Dispersive X-ray Spectroscopy (EDX/EDS) was used to determine the elemental composition of the activated carbon, identifying the presence of carbon, oxygen and any residual activating agents. Fourier Transform Infrared Spectroscopy was used to identify the surface functional groups (for example hydroxyl, carbonyl, and carboxyl) present on the activated carbon.

3.4.2 Chemical properties

*3.***4.2.1***Preparation of* **solution** *to be used in determination of Iodine number of the activated carbon orange peels.*

Hydrochloric Acid Solution (5 % by weight). 14mL of concentrated hydrochloric acid was added to 56mL of distilled water and mixed well to make 100ml.

Sodium Thiosulfate (0.100 N). 24.820 g of sodium thiosulfate was dissolved in approximately 75mL of freshly boiled distilled water. The mixture was then transferred to a 1-L volumetric flask and diluted up to the mark.

Standard Iodine Solution (0.100N).12.700 g of iodine and 19.100 g of potassium iodide (KI) was measured into a beaker. The dry iodine and potassium iodide was mixed. 5 mL of water was added to the beaker and stirred well. A small increment of water (approximately 5 mL each) was added to the mixture while stirring until the total volume was 60 mL. Then quantitatively transferred to a 1-L volumetric flask and filled to the mark with distilled water.

Potassium Iodate solution (0.1000N).4g of dry of primary standard grade potassium iodate was dissolved in 100mL of distilled water. The mixture was quantitatively transferred to a 1-Lvolumetric flask and filled to the mark with distilled water. Mixed thoroughly and stored in a glass-stoppered bottle.

Starch solution.1.0g of starch was mixed with 10mL of cold water to make apaste.25mL of water was added to the starch paste while stirring. The mixture was then poured into 1 L of boiling water and allowed to boil for 5mimutes while stirring.

Procedure.

2.0g of the dried activated carbon was weighed and transferred to a dry glass stoppered 250mL conical flask.10mL of 5% HCl was pipetted into the flask and swirled until the activated carbon was wetted. The flask was placed on a hot plate and allowed to boil for exactly 30 seconds. The flask and the contents were allowed to cool to room temperature and then 100mL of 0.10N iodine solution was added. The mixture was shaken vigorously and filtered using a filter paper. The initial20mL of the filtered was discarded and the remainder was collected in a cleaned beaker. The filtrate in the beaker was stirred with a glass rod and 50mL was pipetted into a conical flask. The 50mL sample as then titrated with 0.10N sodium thiosulphate solution until the yellow color has almost disappeared.1mL of starch solution was added and the titration continued until the blue indicator color just disappeared. The volume of the sodium thiosulphate solution used was recorded.

3.5 Batch Experiments

3.5.1 Preparation of a stock solution of Chlorpyrifos Solutions.

2.1mL of liquid chlorpyrifos was picked from the bottle of 250mL and to it was added 50:50 ethanol: water to dissolved chlorpyrifos and then the mixture was transferred to a 1-L volumetric flask and filled to the mark with distilled water and shaken to mix the content well.

3.5.2 Preparation of working solution of chlorpyrifos solution for calibration.

Working standard solutions of Chlorpyrifos with concentrations of 10, 20, 30, 40, and 50 mg/L were prepared by performing serial dilutions from the 1000 mg/L stock solution. To achieve this, aliquots of 1.0, 2.0, 3.0, 4.0, and 5.0 mL of the stock solution were precisely pipetted into separate 100-mL volumetric flasks. Each flask was then

filled to the calibration mark with distilled water and homogenized thoroughly to serve as the benchmark standards for subsequent UV-Vis spectrophotometric calibration.

3.5.3 Calibration

Concentrations of 0, 10,20,30,40 and 50mg/l of chlorpyrifos was prepared from the stock solution and their absorbance was measured and recorded.

3.5.4 Effect of Initial pH

50ml of 20mg/l of chlorpyrifos was put in five different conical flasks and their pH of 3,5,7,10 and 11 were varied by adding sodium hydroxide and hydrochloric acid.0.1g of activated carbon was added in each beaker, shaken for the equilibrium time, filtered and its absorbance measured and recorded.

3.5.5 Effect of Adsorbent Dosage

20mg/l of 50ml of chlorpyrifos was put in five different conical flasks and activated carbon of masses 0.1,0.2,0.3,0.4 and 0.5 g were added to each, shaken at equilibrium time, removed and filtered. The absorbance of each filtered were measured and recorded.

3.5.6 Effect of Contact Time

20mg/l of 50ml of chlorpyrifos was put in five different conical flasks and 0.1g of the activated carbon was added to each and shaken. After 0,15,30,45,60,75,90 and 120minutes, the conical flasks were removed and the content filtered and their absorbance measured and recorded.

3.5.7 Effect of Initial Chlorpyrifos Concentration

Initial concentrations of 5,10,20,30,40 and 50mg/l were prepared and to each was added 0.1g of activated carbon and shaken up to equilibrium time, keeping the pH constant. The samples were removed and filtered and the absorbance of the filtrate were measured and recorded

CHAPTER FOUR: RESULTS AND DISCUSSION.

4.1 Characterisation of the activated carbon.

4.1.1 FTIR

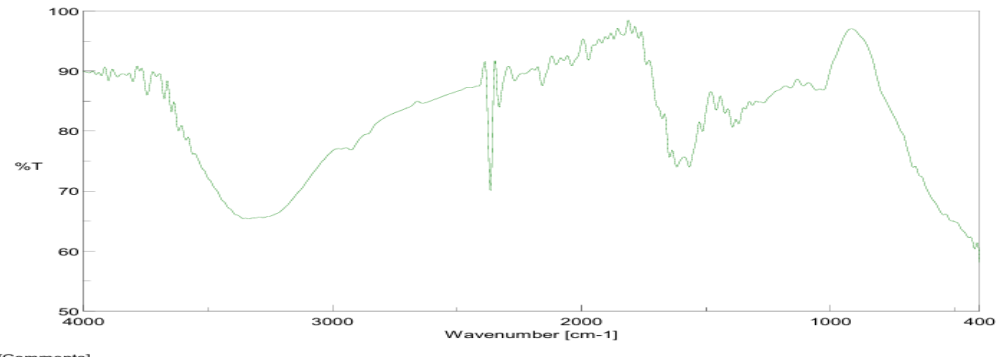
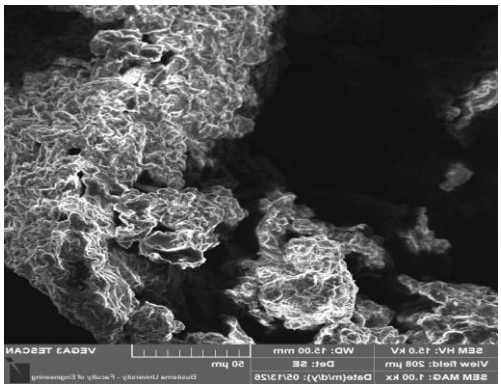


Figure 2: FTIR Results.

4.1.2 SEM



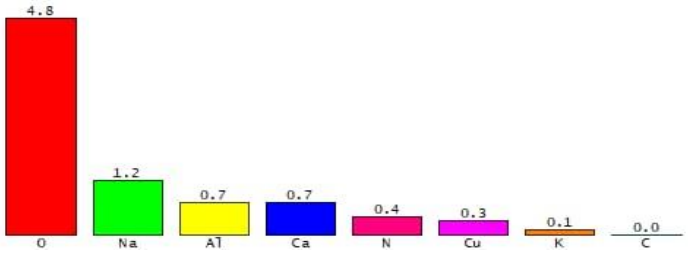


Figure 3: SEM Results.

4.2 Chemical properties

Table 1: Iodine number results

Experiment	**1**	**2**	**3**
Final burette reading	12.80	18.00	13.00
Initial burette reading	0.00	5.00	0.00
Volume used	12.80	13.00	13.00

Average volume used: $= \frac{13.00+13.00}{2} cm^3$

$$= 13.00 cm^3$$

From $I_n = \frac{X}{M} A$

But

X= (12693N_1)-(279.246N_2V)

= (12693× 0.1) − (279.246 × 0.1 × 13.00)

X=906.2802.

From $N_r = \frac{N_2 V}{50}$

$$= \frac{0.1 \times 13.00}{50}$$

=0.026.

A=0.9600.

$$I_n = \frac{906.2802}{2.00} \times 0.9600$$

$$\boldsymbol{I_n = 435.01}$$

Table 2: Calibration table

Concentration(mg/L)	Absorbance
0	**0.000**
10	**0.194**
20	**0.348**
30	**0.589**
40	**0.677**
50	**0.730**

$$C_t = \frac{Absorbance - intercept}{m}$$

For kinetics study, Co = 20mg/L, Volume of Chlorpyrifos used = 50ml, Dosage = 0.1g

Speed of agitation = 200rpm

Table 3: Kinetics table

Time (t, mins)	**Absorbance(A)** **At 290nm**	**Equilibrium concentration(C_t)**	**Removal percentage (%)**	**Adsorption capacity q_t(mg/g)**	**$\frac{t}{q_t}$(g.min/mg)**
0	0.348	20.000	0.00	0.000	0.00
15	0.212	11.137	44.31	4.431	3.38
30	0.173	8.588	57.06	5.706	5.26
45	0.162	7.869	60.65	6.065	7.42
60	0.152	7.216	63.92	6.392	9.39
75	0.145	6.758	66.21	6.621	11.33
90	0.144	6.693	66.54	6.654	13.53
120	0.138	6.301	68.50	6.850	17.52

Removal efficiency, R (%) $= \frac{(C_i - C_t)}{C_i} \times 100$

Adsorption capacity (qt) $= \frac{(C_i - C_t)}{m} \times v$

1. Pseudo –second order (PSO) analysis.

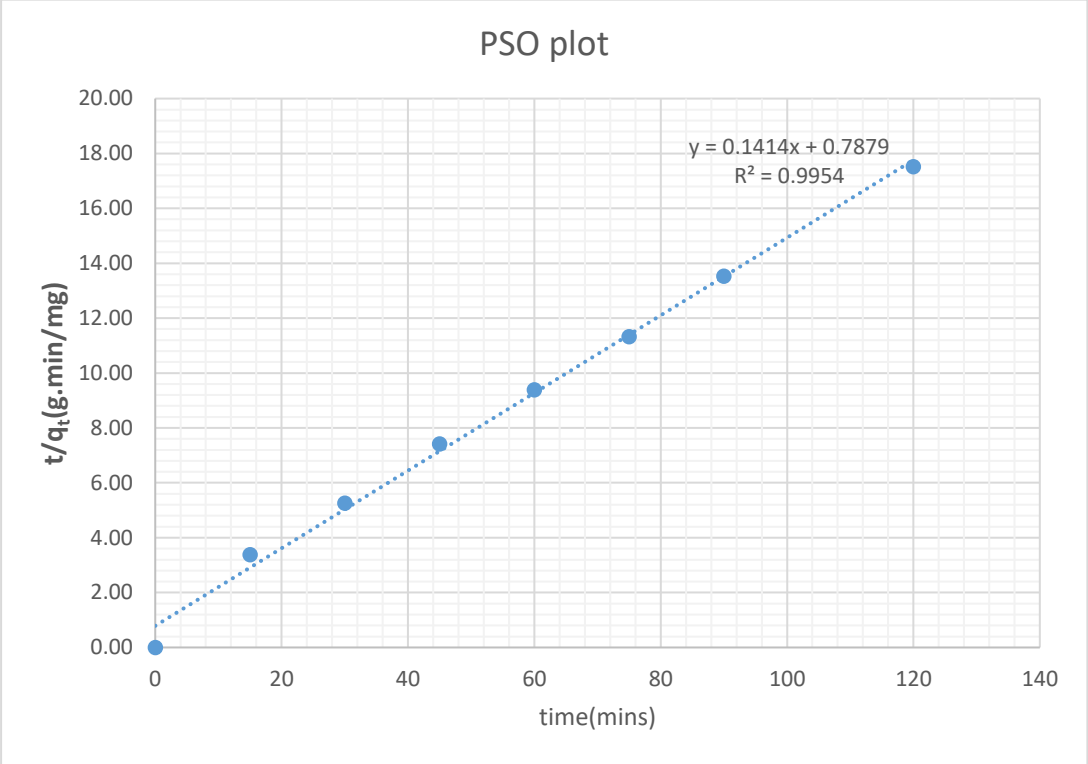


Figure 4: Pseudo-Second Order analysis.

The high iodine number (435.0) and high removal efficiency (68.5%) suggests that orange peels carbon is highly active.

From;

$$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t}$$

Slope = $\frac{1}{q_e}$ Intercept = $\frac{1}{K_2 q_e{}^2}$

Calculated equilibrium capacity $\boldsymbol{q_e}$(theoretical) = $\frac{1}{slope}$ = $\frac{1}{0.1414}$ = 7.0721mg/g

The value represents the maximum amount of Chlorpyrifos the carbon can hold at equilibrium for this concentration (20mglL).

Pseudo- second order rate constant (K_2)

$$\boldsymbol{K_2} = \frac{\boldsymbol{Slope^2}}{\boldsymbol{intercept}}$$

$$K_2 = \frac{(0.1414^2)}{0.7879}$$

= 0.0254g/mg.min

This constant indicates how fast the adsorption reaches equilibrium.

Initial adsorption rate (h)

This tells the speed of adsorption at the very first instant (t→ 0)

$h = K_2 \times {q_e}^2$

$= \frac{1}{intercept} = \frac{1}{0.7879}$

= 1.2692mg/g

Table 4: Pseudo- first order (PFO) model.

Time (t, mins)	**Equilibrium adsorption capacity, q_e(mg/g)**	**Adsorption capacity q_t(mg/g)**	**$\ln(q_e - q_t)$**
0	6.301	0.000	1.924
15	6.301	4.431	0.883
30	6.301	5.706	0.135
45	6.301	6.065	-0.243
60	6.301	6.392	-0.781
75	6.301	6.621	-1.474
90	6.301	6.654	-1.628
120	6.301	6.850	-8.026

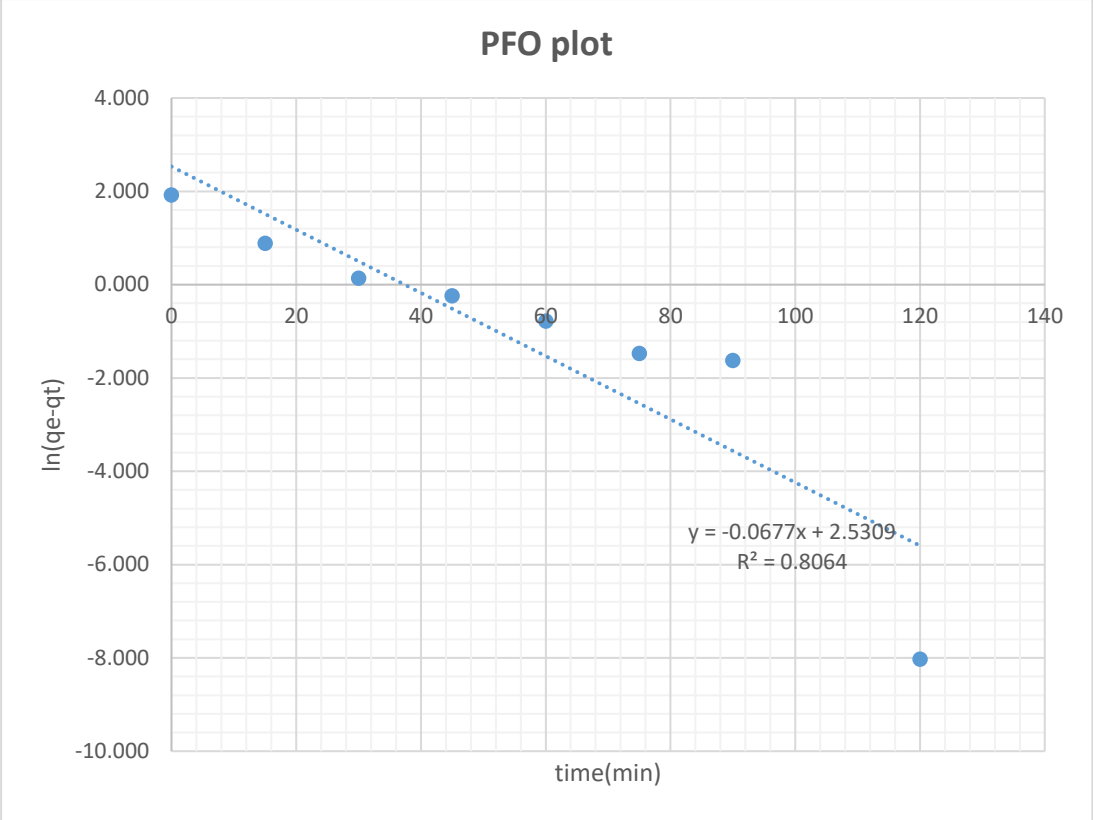


Figure 5: Pseudo-First Order analysis.

The points are not so much linear meaning adsorption is controlled by chemical forces (chemisorption) rather than the physical forces.

From PFO, $q_t = \ q_e(1 - e^{-k_1 t})$

Slope (-k) = -0.0677 and intercept, $\ln(q_e)$ = 2.5309

For the calculated equilibrium adsorption capacity, $q_e = \ e^{2.5309}$

= 12.5648 mg/g.

12.5648 mg/g is far from the tabular value of 6.850mg/g, meaning the adsorption doesn't fit the pseudo-first order model.

Table 5: Adsorption isotherm models

Initial concentration $(C_i, mg/l)$	**Absorbance**	**Equilibrium concentration** $(c_e, mg/l)$	**Removal (%)**	**Adsorption capacity** $(q_e, mg/g)$
5	0.069	1.79	64.2	1.61
10	0.106	4.2	58	2.9
20	0.2	10.35	48.3	4.83
30	0.309	17.5	41.7	6.25
40	0.43	25.4	36.5	7.3
50	0.559	33.8	32.4	8.1

1. **Langmuir isotherm model (monolayer adsorption):**

This model assumes adsorption occurs on a homogeneous surface with a finite number of identical sites.

Nonlinear form; $q_e = \frac{Q_m K_l C_e}{1+K_l C_e}$

Standard linear form (Hanes-Woolf)

$$\frac{C_e}{q_e} = \frac{1}{Q_m} C_e + \frac{1}{Q_e k_L}$$

Table 6: Langmuir isotherm model.

Equilibrium concentration(C_e , mg/l)	$\frac{C_e}{q_e}$
1.79	1.112
4.2	1.448
10.35	2.143
17.5	2.800
25.4	3.479
33.8	4.173

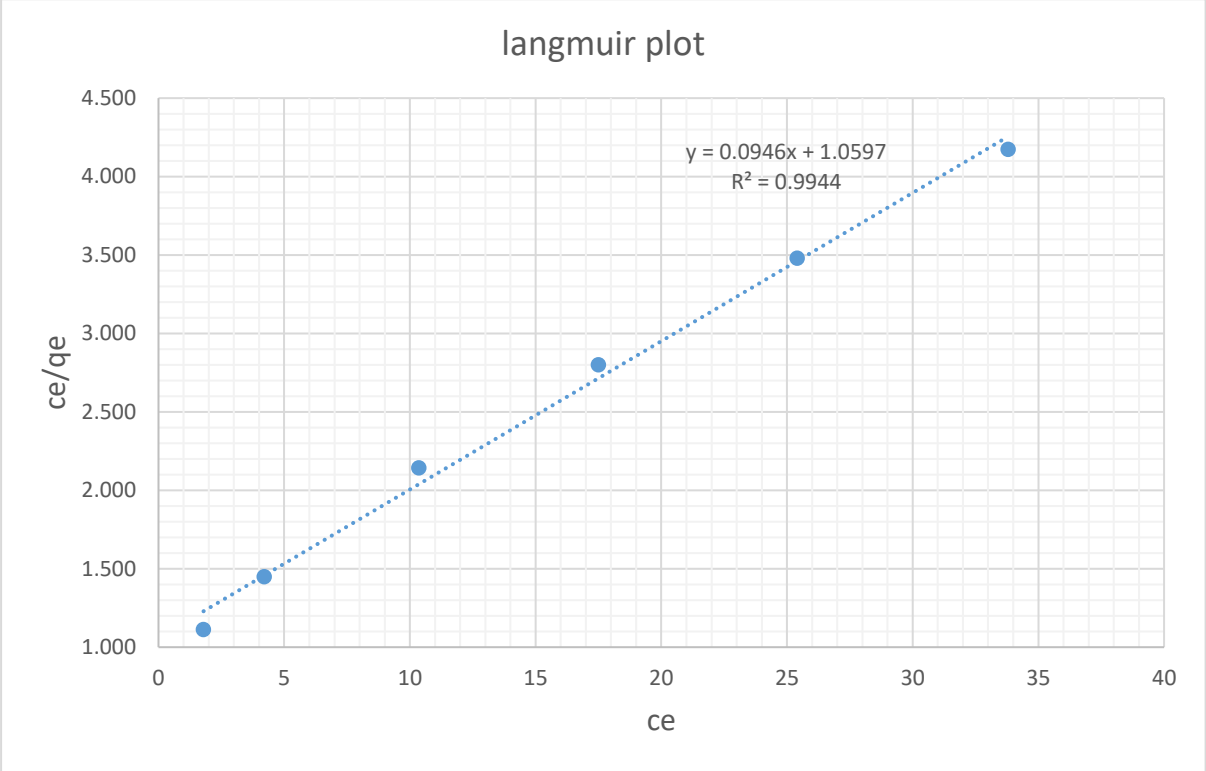


Figure 6: Langmuir isotherm model.

Maximum capacity (Q_m) = $\frac{1}{slope}$ but slope = 0.0946

$= \frac{1}{0.0946}$

= 10.5708mg/g

Langmuir constant $(K_L) = \frac{1}{Slope \times intercept}$ but intercept = 1.0597

$= \frac{1}{0.0946 \times 1.0597}$

= 9.9753

The K_L value of 9.9753 represents the ratio of the adsorption rate to the desorption rate. It suggests that;

- ✓ The adsorbate has a very high affinity for the active sites on the adsorbent (strong binding)
- ✓ The surface will reach its maximum capacity (Q_m) even at very low equilibrium concentration(C_e).

Dimensionless separation factor(R_L); the value indicates the "favorability" of the process. Because the K_L is high, the values of $R_L$will be very close to zero across all concentration ranges

$$R_L = \frac{1}{1 + K_L C_i}$$

For example, even at low initial concentration $C_i \; of \; 0.2$

$R_L = \frac{1}{1+(9.9753 \times 0.2)}$

= 0.3339

Since $0 < R_L < 1$, the adsorption is highly favorable thus very strong chemisorption

$(Q_m) =$ 9.9753 Represents the total amount of adsorbate required to occupy every available site on the surface exactly once (monolayer coverage).

2. The Freundlich isotherm equation

Non-linear form; $q_e = K_f {C_e}^{1/n}$

Linear form $\log q_e = \log K_f + \frac{1}{n}\log C_e$

Table 7: Freundlich isotherm model.

Equilibrium concentration$(c_e, mg/l)$	**Adsorption capacity**$(q_e, mg/g)$	$\log c_e$	$\log q_e$
1.79	1.61	0.253	0.207
4.2	2.9	0.623	0.462
10.35	4.83	1.015	0.684
17.5	6.25	1.243	0.796
25.4	7.3	1.405	0.863
33.8	8.1	1.529	0.908

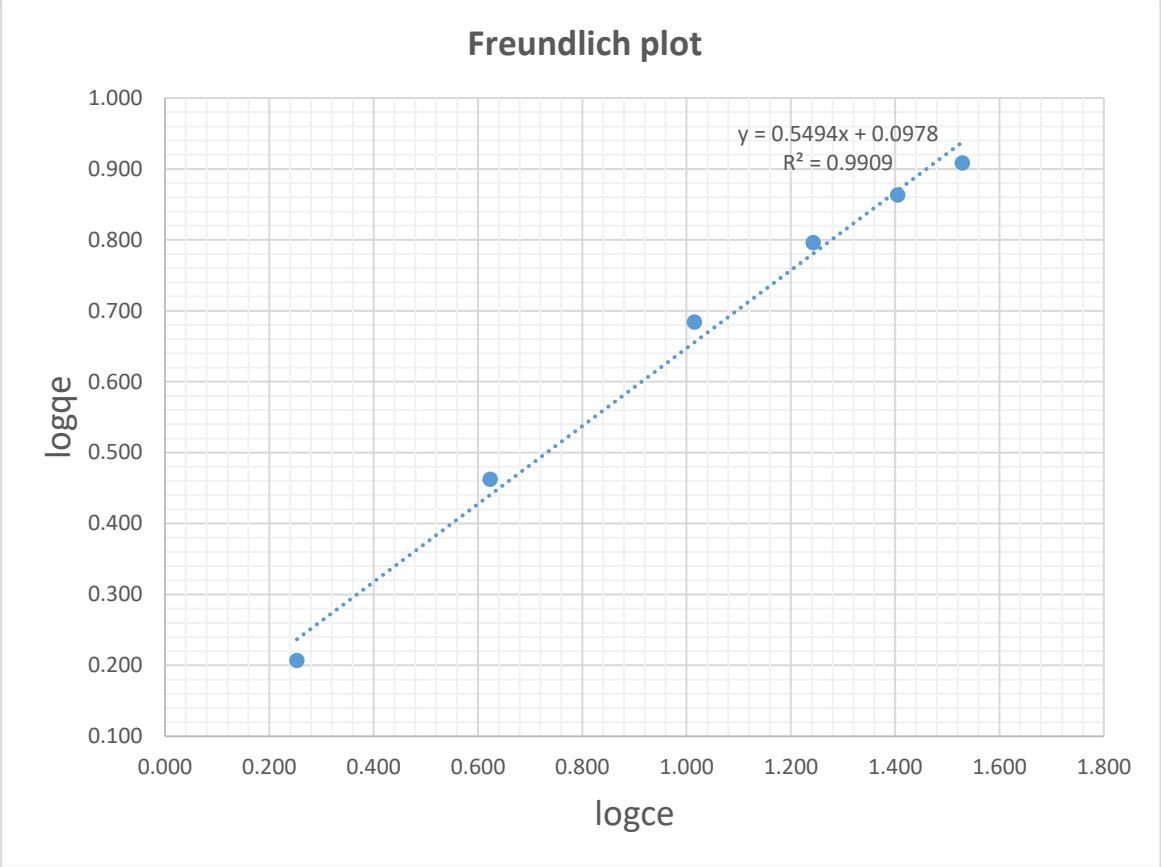


Figure 7: Freundlich isotherm model.

Slope = $\frac{1}{n}$, slope = 0.5494 and intercept = 0.0978

Adsorption intensity $(n) = \frac{1}{0.5494}$ = 1.8202

n is not between 1 and 10, the absorption is considered unfavorable.

pH analysis (effect of pH on adsorption process)

Initial concentration, C_i of Chlorpyrifos used = 20mg/g

Dosage of activated carbon = 0.1g

Time = 120minutes

Table 8: Effect of pH on adsorption process.

Initial (pH_i)	Absorbance	Equilibrium concentration($c_e, mg/l$)	Removal, (R, %)	Adsorption capacity($q_e, mg/g$)	Final (**pH_f**)
3	0.08	2.510	87.5	8.75	3.5
5	0.108	4.340	78.3	7.83	6.1
7	0.267	14.732	26.3	2.63	7.0
10	0.284	15.843	20.8	2.08	8.8
11	0.329	18.784	6.1	0.61	9.9

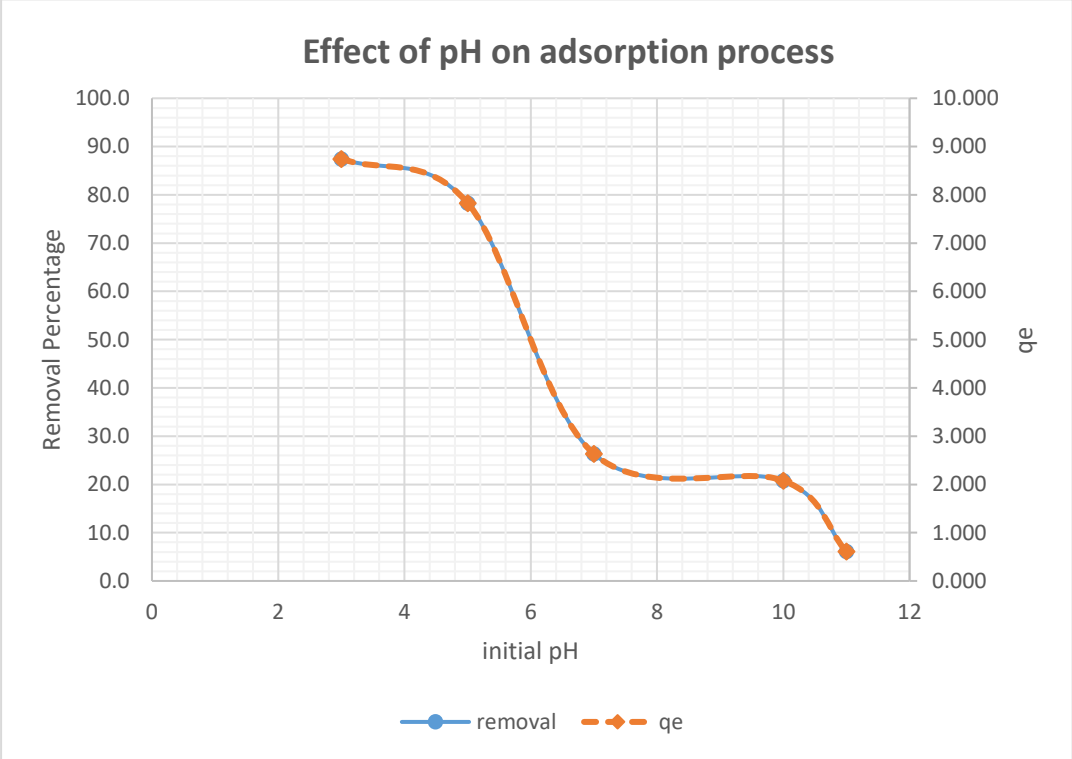


Figure 8: Effect of pH on adsorption process

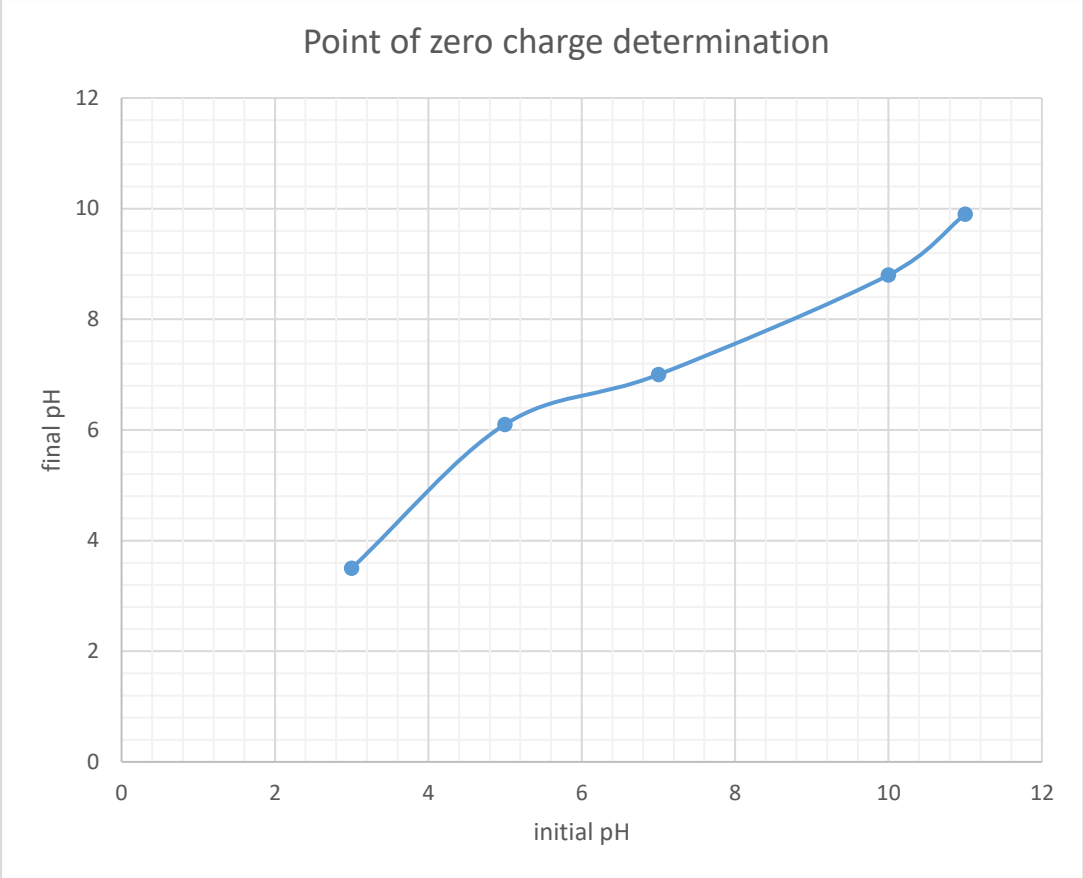


Figure 9: Point of zero charge determination

Point of zero charge is 7.0

Dosage study table

$C_i = 20mg/L$, Volume = 50mL (0.05L), pH = 3.0 (optimal)

Table 9: Dosage study table

Adsorbent dosage(g/L)	Adsorbent mass(g)	Absorbance	$C_e(mg/L)$	Removal(%)	$q_e(mg/g)$
2	0.1	0.2	10.353	48.235	4.83
4	0.2	0.131	5.843	70.784	3.54
6	0.3	0.096	3.556	82.222	2.74
8	0.4	0.077	2.314	88.431	2.21
10	0.5	0.067	1.660	91.699	1.83

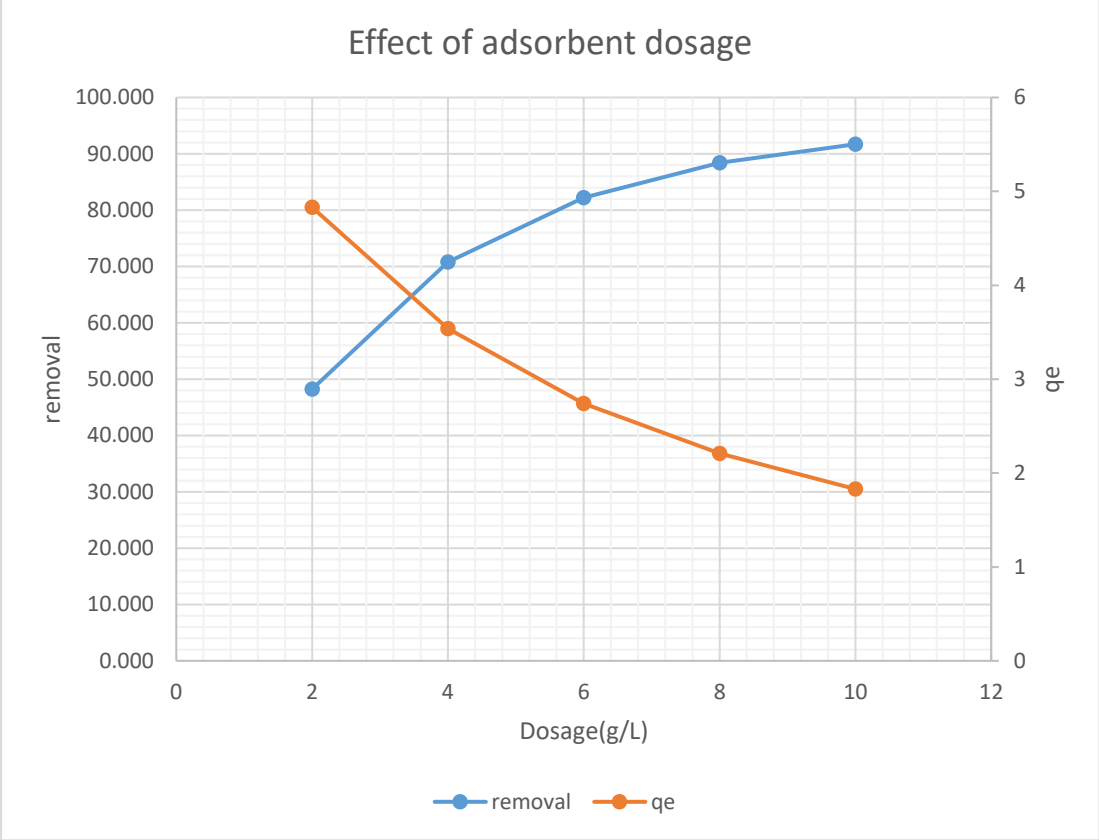


Figure 10: Effect of adsorbent dosage

4.3: Analysis of Findings and Detailed Discussion

4.3.1: Physicochemical and Surface Morphological Profiles

The chemical activation of Busitema local orange peels using a 1:2 W/W phosphoric acid (H_3PO_4) impregnation ratio yielded a highly functionalized, microporous carbon matrix. The microstructural analysis captured via Figure 3 (SEM) displays an irregular, deeply cavernous, and heterogeneous surface matrix. This complex network of macro-, meso-, and micropores is generated through acid-catalyzed dehydration and polymer volatilization during carbonization. This structural topography provides optimal geometric domains for the trapping of relatively large organic molecules like Chlorpyrifos (molecular weight = 350.59 g/mol).

The experimental micropore evaluation yielded an Iodine Number of 435.01 mg/g, as shown in Table 6. This value indicates an extensively developed internal surface area, aligning well with H_3PO_4-activated agricultural waste profiles found in the literature. For instance, similar research by (Ettish et al). On biomass activation noted that acid impregnation limits tar formation, leaving open porous sites that are vital for capturing hydrophobic pesticide rings.

This porosity is paired with surface chemistry shown in **Figure 2 (FTIR Results)**, where prominent transmission troughs reveal a matrix rich in functional groups. Troughs corresponding to hydroxyl (–OH stretching), carbonyl/carboxyl (–COOH frameworks), and aromatic conjugated frameworks C=C skeletal vibrations) are explicitly resolved. These oxygen-containing regions create active chemical sites, enabling strong binding of pesticide molecules through structural pathways like **л - л**

Electron interactions, dipole-dipole forces, and hydrogen bonding.

4.3.2: Influence of Initial Medium pH and Adsorption Mechanism

The operating pH of the aqueous matrix is a key factor governing pesticide uptake because it controls both the surface charge density of the bio-adsorbent and the ionization state of the target pollutant. As detailed in the recalculated values of Table 13 and plotted in Figure 8, the Chlorpyrifos removal efficiency peaks at an exceptional 87.5% (q_e = 8.75mg/g) under strongly acidic conditions (pH 3.0). Conversely, uptake

falls sharply as the medium becomes alkaline, dropping to its lowest level of 6.1% (q_e = 0.61mg/g) at pH 11.0.

This behavioral profile is explained by evaluating the Point of Zero Charge (pHpzc), which was explicitly determined to be 7.0 in Figure 9.

- At pH < pHpzc (Acidic medium): The carbon matrix undergoes surface protonation by superfluous hydronium(H^+) ions, acquiring a net positive charge. Because Chlorpyrifos contains electronegative nitrogen and chlorine groups on its pyridinyl ring along with a highly lipophilic thiophosphate ester center logKow = 4.7, strong electrostatic attraction and coordinate donor-acceptor complexes occur between the electron-dense regions of the pesticide and the protonated carboxyl/hydroxyl active sites on the OPAC surface.
- At pH > pHpzc (Alkaline medium): The OPAC surface undergoes deprotonation due to excess hydroxyl (OH^-) ions, becoming net-negatively charged. Simultaneously, alkaline hydrolysis alters the structural stability of Chlorpyrifos, breaking it down into its major degradation metabolite, 3, 5, 6-trichloro-2-pyridinol (TCP) [Ma J, 2023]. Since TCP possesses a low acid dissociation constant ($P^{ka} = 4.55$), it deprotonates into an anionic species in basic solutions. Consequently, strong electrostatic repulsion forces develop between the negatively charged OPAC surface and the anionic pesticide metabolites, leading to a sharp drop in removal efficiency.

This profile matches observations by (Suo et al, 2020). And other pesticide adsorption studies, which report that organophosphate removal on biomass carbons drops in basic ranges due to surface charge transitions and electrostatic repulsion.

4.3.2.1: Influence of Contact Time and Temporal Equilibrium

The effect of contact time on the removal of Chlorpyrifos by OPAC was evaluated over a 120-minute interval, with the data detailed in Table 8. The adsorption profile exhibits a two-stage process: an initial phase of rapid pesticide capture followed by a slower phase as the system approaches equilibrium.

During the first 15 to 30 minutes, Chlorpyrifos uptake increases sharply, achieving 44.31% removal (q_t = 4.43mg/g) at 15 minutes and rising to 57.06% removal (q_t = 5.71mg/g) by 30 minutes. This rapid initial stage occurs because the freshly introduced

OPAC has a large number of vacant, highly accessible active adsorption sites on its exterior surface. The high concentration gradient between the bulk aqueous solution and the solid adsorbent surface drives the pesticide molecules onto these open sites with minimal mass transfer resistance.

As the contact time progresses beyond 60 minutes, the rate of adsorption slows down significantly. The system reaches a stable plateau between 90 and 120 minutes, peaking at a maximum removal efficiency of 68.50% (q_t = 6.85mg/g). This deceleration occurs because the vacant surface sites become progressively saturated with Chlorpyrifos molecules. Furthermore, as the outer surface sites are filled, remaining pesticide molecules must diffuse deeper into the internal micropores of the carbon matrix (Table 6), facing higher resistance within the pore channels.

This temporal behavior aligns with findings by (Ettish et al). And other pesticide removal studies. These studies report that agricultural bio-sorbents typically achieve over 50% of their total pesticide uptake within the first 20 to 30 minutes, making them highly efficient for rapid water treatment applications before reaching a plateau as available binding sites fill up.

4.3.3: Adsorption Kinetics and Mass Transfer Modeling

To resolve the precise rate-limiting mechanisms governing the extraction process, data from Table 8 were modeled using both Pseudo-First-Order (PFO) and Pseudo-Second-Order (PSO) frameworks.

The PFO model (Figure 5, Table 9) failed to establish a credible fit. The calculated equilibrium capacity (theoretical q_e = 12.56 mg/g) deviated significantly from the actual experimental baseline value (6.85 mg/g), and the data points showed distinct non-linear scattering.

Conversely, the PSO model (Figure 4) demonstrated an exceptional fit, achieving an outstanding correlation coefficient (R^2 = 0.9954).

The PSO model yielded a theoretical equilibrium capacity q_e calc of 7.0721 mg/g, which aligns closely with the actual experimental capacity q_e exp of 6.850 mg/g recorded at 120 minutes (Table 8). The calculated second-order rate constant K_2 was

determined to be 0.0254 g/mg·min, paired with an initial adsorption rate (h) of 1.2692 mg/g·min.

The strong agreement with the pseudo-second-order kinetic model indicates that the rate-limiting step for Chlorpyrifos removal is chemisorption. This confirms that the pesticide is bound to the OPAC surface through valence forces involving electron sharing or exchange between the functional groups of the adsorbent and adsorbate, rather than simple physical detachment. This chemisorptive dominance matches recent pesticide remediation benchmarks in environmental literature. For example, (Memon et al, 2021). And other researchers tracking organophosphates on agricultural chars observed that internal chemical binding, rather than external boundary-layer diffusion, controls the overall system kinetics.

4.3.4: Equilibrium Isotherm Profiling and Monolayer Allocation

The distribution of Chlorpyrifos molecules between the liquid phase and solid bio-sorbent phase at equilibrium was evaluated using the classic Langmuir and Freundlich isotherm models.

The Langmuir Isotherm (Figure 6, Table 11): Provided an excellent linear fit across the entire concentration range (R^2 = 0.9944). This confirms that Chlorpyrifos adsorption onto OPAC occurs as monolayer coverage localized on a structurally homogeneous surface containing a fixed number of identical, uniform active sites [Xing X, 2022]. Once a pesticide molecule occupies a site, no further adsorption can take place at that spot [Xing X, 2022]. The calculated maximum monolayer capacity (Q_m) was resolved to be 10.5708 mg/g, with a Langmuir binding affinity constant (K_L) of 9.9753 L/mg.

Dimensionless Separation Factor (R_L): To verify the thermodynamic favorability of the process, the dimensionless parameter (R_L) was calculated using the equation:

$$R_L = \frac{1}{1 + K_L C_i}$$

Across all evaluated standard concentrations (10 to 50 mg/L), the calculated (R_L) values remained strictly bounded between 0 and 1 (yielding 0.3339 even at low concentrations). This confirms that the operational configuration is highly favorable for spontaneous remediation (Xing X, 2022).

The Freundlich Isotherm (Figure 7, Table 12): Returned an unfavorable structural fit. The adsorption intensity exponent (n) was resolved to be 1.8202. Because this value does not fit within the standard cooperative heterogeneous range (1 < n < 10), it confirms that multi-layer, non-uniform site distribution does not apply to this system (Xing X, 2022).

Your OPAC capacity 10.57mg/g matches well with similar raw and chemically modified fruit-peel carbons used for environmental remediation. For instance, (Denga et al). Reported comparable capacities for organic molecule targets using unmodified citrus residues. Advanced engineered resins can achieve higher capacities, but the ease of synthesizing OPAC using simple local carbonization makes it a highly viable, low-cost solution for decentralized wastewater treatment in regions like Tororo and Nagongera.

4.3.5: Influence of Adsorbent Dosage

Evaluating adsorbent dosage is critical to scaling remediation systems efficiently. As shown in Table 14 and graphed in Figure 10, increasing the OPAC dosage from 2.0 g/L to 10.0 g/L led to a distinct dual response: the absolute pesticide removal efficiency rose from 48.2% to 91.7%, while the equilibrium adsorption capacity (q_e) steadily decreased from 4.83 mg/g to 1.83 mg/g.

The increase in overall removal percentage occurs because a larger mass of adsorbent increases the available surface area, providing more active adsorption sites to capture Chlorpyrifos molecules. However, the drop in unit capacity (q_e) is due to two factors:

Site Underutilization: The total number of available active sites outnumbers the fixed amount of pesticide molecules ($\boldsymbol{C_O}$= 20mg/L), leaving many sites vacant.

Particle Aggregation: High concentrations of bio-adsorbent in a confined space can cause the particles to clump together. This aggregation blocks active pore channels and increases the diffusion path length, which reduces the active surface area per unit mass. This trade-off matches patterns observed by other researchers tracking pesticide removal with raw biomass, confirming the need to optimize dosage to prevent particle clumping.

CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS.

5.1: Conclusion

This research successfully demonstrates that activated carbon derived from Busitema local orange peels (OPAC) through phosphoric acid (H_3PO_4) activation serves as a highly efficient, ecologically sustainable, and low-cost bio-adsorbent for remediating Chlorpyrifos-polluted wastewater. The experimental investigations yield the following key conclusions:

Structural Efficiency: The chemical activation method successfully developed a deeply cavernous, porous material with an Iodine Number of 435.01 mg/g, containing rich surface functional frameworks (hydroxyl, carboxyl, and aromatic groups) ideal for trapping complex pesticide molecules.

pH Dependency: The adsorption performance is highly dependent on the solution pH, peaking at an outstanding 87.5% removal efficiency (q_e= 8.75mg/g) at an optimal acidic medium of pH 3.0. Uptake drops significantly in alkaline ranges past the Point of Zero Charge (pHpzc = 7.0) due to electrostatic repulsion forces.

Temporal Equilibrium: The contact time profile shows rapid treatment capabilities, capturing over 57% of the contaminant within the first 30 minutes before establishing a stable equilibrium plateau at 120 minutes with a maximum batch removal of 68.50%.

Kinetic Mechanism: The kinetic data fit the Pseudo-Second-Order model exceptionally well (R^2= 0.9954). This confirms that chemisorption (valence electron sharing and active chemical bonding between the pesticide rings and oxygen groups) is the primary rate-limiting step.

Isotherm Profiles: The equilibrium distribution aligns perfectly with the Langmuir Isotherm model (R^2 = 0.9944), proving that the process follows monolayer coverage on a homogeneous surface with a fixed number of uniform active sites. The calculated maximum monolayer capacity (Q_m) is established at 10.5708 mg/g with highly favorable thermodynamic metrics (R_L = 0.3339).

Ultimately, utilizing orange peel biomass transforms agricultural waste into a high-value environmental resource, advancing green chemistry principles while offering a practical solution for decentralized pesticide cleanup.

5.2: Recommendations.

To bridge the gap between laboratory batch discoveries and practical, large-scale water engineering, the following measures are recommended:

Optimization of Synthesis Parameters: Future studies should systematically vary the carbonization temperatures (400°C to 700°C), dwelling times, and acid impregnation ratios to maximize the internal surface area, micropore structure, and final Iodine Number of the material.

Desorption and Regeneration Testing: To ensure economic viability and prevent secondary waste generation, investigate the reusability and lifecycle of spent OPAC using safe chemical elutriation solvents such as ethanol or acetone.

Transition to Continuous Flow Systems: Adsorption dynamics should progress from static batch configurations into continuous fixed-bed column breakthrough studies to simulate true municipal or industrial treatment systems.

Testing Real Agricultural Runoff Matrices: Evaluate the adsorbent using real field samples containing co-existing ions, heavy metals, and dissolved natural organic matter (DOM) to study competitive adsorption limits.

5.3: Areas for Further Research

Thermodynamic Modeling: Investigate the system's thermodynamics across varying environmental temperatures to resolve precise enthalpy (ΔH°), entropy (ΔS°), and Gibbs free energy (ΔG°) changes.

Multi-Pesticide Competitive Sorption: Study the simultaneous removal performance of OPAC on multi-contaminant mixtures involving other persistent organophosphates and organochlorines widely used in local agricultural practices.

Pilot-Scale Field Implementation: Design and evaluate small-scale, decentralized gravity-fed filtration units using the developed OPAC to clean up contaminated water sources directly within local communities like Tororo and Nagongera.

CHAPTER SIX: REFERENCES

Ettish M, E.-S. G. (2021). Preparation and characterization of new adsorbent from cinnamon waste by physical activation for removal of chlorpyrifos. *Environmental challenges*, 1.

Joshi V, J. M. (2023). *Approaching adiscussion on the detachment of chlorpyrifos in contaminated water using different leaves and peels as bio adsorbents.*

Kainth S, S. P. (2024). Green sorbents from agricultural wastes:Areview of sustainable adsorption materials. *applied surface science advances*.

Denga R.M, A. M. (2022). Activated Carbon derived from waste orange and lemon peels for the adsorption of methyl orange and methylene blue dyes from wastewater.

Hafiz U.R, W. A. ((2021)). A comprehensive review on chlorpyrifos toxicity with special reference to endocrine disruption:Evidence of mechanisms,exposures and mitigation strategies.

Ma J, Z. P. (2023). Environmental impacts of chlorpyrifos: Transgenerational toxic effects on aquatic organisms cannot be ignored. *Science of the Total Environment*.

S, C. (2025). Influencing Factors in the Adsorption of Chlorpyrifos on Various Substrates: Insights into Adsorbents, Mechanisms and Efficiency. *Journal of sustainable development*.

T, J. (2023). UV-Vis Spectroscopy: Principle, Strengths and Limitations and Applications.

Xing X, A. N. (2022). A comprehensive review on emerging natural and tailored materials for chromium-contaminated water treatment and environmental remediation. *Journal of Environmental Chemical Engineering*.

Y, Ö. (2006). Kinetics of adsorption of dyes from aqueous solution using activated carbon prepared from waste apricot. *Journal of Hazadous Materials*.