https://chemclassjournal.com/
ChemClass Journal Vol. 9 Issue 3 (2025); 80 - 103
e-ISSN:3092-8214 p-ISSN:3092-8206
doi.org/10.33003/chemclass-2025-0903/07

Removal of Oxytetracycline from Aqueous Solution Using Activated Carbon Derived from *Eichhornia crassipes* (Water Hyacinth): Kinetics, Isotherm, and Thermodynamic Studies

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Abstract

This research investigates the efficacy of activated carbon (AC) derived from water hyacinth (WH) for the removal of dissolved organic matter (DOM), specifically oxytetracycline (OTC), from aqueous solutions. Water hyacinth, a prolific aquatic weed, was carbonized and chemically activated with hydrochloric acid to produce a low-cost adsorbent (WHAC). The adsorbent was characterized using Scanning Electron Microscopy (SEM), which revealed a porous, weave-like structure, and Fourier Transform Infrared Spectroscopy (FTIR), which identified key functional groups. Batch adsorption studies were conducted to evaluate the effects of operational parameters. Optimal OTC removal was achieved at an adsorbent dose of 0.1 g, pH 5, a contact time of 150 minutes, and a temperature of 60°C. Equilibrium data were best described by the Langmuir isotherm model, indicating monolayer adsorption, with a maximum adsorption capacity of 115.4 mg/g. Kinetic studies confirmed that the adsorption process followed a pseudo-second-order model. Thermodynamic parameters (negative ΔG, positive ΔH) revealed that the adsorption was spontaneous and endothermic. The study concludes that activated carbon prepared from water hyacinth is an effective, economical, and eco-friendly adsorbent for removing organic pollutants like oxytetracycline from wastewater, offering a valuable solution for both wastewater treatment and the management of an invasive aquatic species.

Keywords: Adsorption, Activated Carbon, Isotherm, Kinetics, Oxytetracycline, Water Hyacinth

Introduction

One of the most urgent problems of the twenty-first century is the threat of environmental pollution, especially water contamination, which directly jeopardizes ecological integrity and public health worldwide. An ever-growing range of toxins has been introduced into aquatic ecosystems as a result of the unrelenting advances in urbanization, industrialization, and intensive farming activities. Pharmaceuticals, personal care items, and endocrine-disrupting chemicals are examples of pollutants of emerging concern

(PECs), which have attracted a lot of scientific and regulatory attention because of their persistence, capacity for bioaccumulation, and subtle yet significant effects on living things [1]. These micropollutants are widely found in surface water, groundwater, and even drinking water supplies worldwide due to the basic organic and nutrient removal capabilities of the conventional wastewater treatment infrastructure [2].

Pharmaceutical chemicals provide a particularly pernicious hazard within the broad group of PECs. Because of their innate ability to trigger a biological reaction, even minute amounts in the environment have the potential to disturb aquatic life and fuel the worrying increase in antimicrobial resistance (AMR), which the World Health Organization has identified as a major threat to global health [3]. One of the most common medications found in water bodies are antibiotics, which are essential to contemporary medicine. Several factors contribute to their release, including the excretion of unmetabolized chemicals by people and animals, inappropriate medicine disposal, and wastewater discharge from pharmaceutical manufacturing facilities [4]. Once in the environment, they encourage the growth and spread of resistance genes by applying selective pressure to microbial communities.

Because of its effectiveness and affordability, oxytetracycline (OTC), a broad-spectrum tetracycline antibiotic, is widely used in aquaculture, veterinary medicine, and human medicine. However, it has a considerable environmental persistence due to its structural stability and resistance to full biodegradation. OTC has been found at quantities ranging from mg/L to µg/L in a variety of water matrices [5]. Chronic exposure carries serious dangers, even though these levels are sub-therapeutic. These risks include toxicity to aquatic plants, the unquestionable promotion of tetracycline-resistant bacteria, and disturbance of native microbial communities that are crucial for nutrient cycling [6]. Therefore, eliminating such resistant chemical compounds from water is not just a technological problem but also a pressing environmental necessity.

The investigation of enhanced oxidation processes, membrane filtration, reverse osmosis, and biological degradation has resulted from the search for efficient remediation solutions. The creation of hazardous byproducts, high operating costs, energy intensity, and limited effectiveness against particular contaminants are some of the drawbacks that these techniques frequently face [7]. Because of its ease of use, affordability, high efficiency, operational adaptability, and overall lack of hazardous byproducts, adsorption has become a leading technique in this regard. The adsorbent, a substance that has a strong affinity for the target pollutant, is essential to this process. The gold standard adsorbent for treating water and wastewater is still activated carbon (AC), which is well-known for its rich surface chemistry, customizable pore structure, and extraordinarily high surface area. It is widely known to be effective in eliminating a variety of contaminants, such as heavy metals, dyes, and organic pollutants [8]. However, the high cost of manufacture and the resulting environmental impact of its sourcing and manufacturing limit the widespread use of commercial activated carbon (CAC), which is usually produced from non-renewable sources like coal or peat. Due to this financial obstacle, there is now intense interest in creating sustainable, affordable, and effective alternative adsorbents using waste and renewable biomass precursors [9].

The "waste-to-wealth" notion offers a convincing framework for dealing with resource management and pollution. Under this paradigm, biomass wastes that are plentiful, troublesome, or underutilized are turned into valuable goods like activated carbon. This method contributes to a circular economy by providing a sustainable waste management solution in addition to lowering the cost of adsorption technology. Coconut shells, rice husks, nutshells, algae, and other aquatic and agricultural wastes have all been effectively transformed into efficient adsorbents [10].

The water hyacinth (*Eichhornia crassipes*) offers a particularly alluring prospect among the many possible biomass choices. This free-floating aquatic macrophyte is indigenous to the Amazon basin, but in tropical and subtropical areas it has emerged as one of the most invasive and damaging weed species globally. Because of its rapid growth rate and the abundance of nutrients in contaminated waters, it can create dense mats that seriously harm aquatic ecosystems. According to Villamagna and Murphy [11], these mats reduce dissolved oxygen, obstruct sunlight, and make it difficult to navigate, interfere with fishing, hinder the production of hydroelectric power, and serve as breeding grounds for mosquitoes and other disease-carrying insects. Conventional management techniques, such mechanical harvesting and chemical herbicides, are frequently expensive, time-consuming, and provide only short-term respite, occasionally with adverse ecological consequences.

As a result, using this problematic biomass to produce activated carbon is a smart two-pronged approach that helps control and manage an invasive species while also producing a useful resource for environmental cleanup. The biomass of water hyacinth is a good lignocellulosic precursor for carbonaceous materials because it is high in cellulose, hemicellulose, and lignin. Through thermochemical processes like pyrolysis and activation, its natural structure can be changed into a porous carbon matrix with a sizable surface area [12]. Prior research has shown that activated carbon and biochar made from water hyacinth can be used to adsorb colors like methylene blue and heavy metals like Pb(II), Cd(II), and Cr(VI) [13]. Nonetheless, there is still much to learn about its use in the removal of intricate medicinal compounds like antibiotics as well as the in-depth analysis of the adsorption processes, kinetics, and thermodynamics involved.

The effectiveness and economic feasibility of the adsorption process itself are determined by a wide range of interconnected factors. The initial concentration of the pollutant, which drives the concentration gradient as the primary force for adsorption; the adsorbent's dosage, which determines the number of available active sites; the pH of the solution, which controls the adsorbent's surface charge and the ionization state of the adsorbate molecule; the amount of time needed to reach equilibrium; and the system temperature, which affects the process's kinetics and thermodynamic viability are all important operational factors [14]. Optimizing the adsorption system for practical uses requires a methodical examination of these characteristics.

Furthermore, comprehending the underlying mechanisms requires interpreting the adsorption data using reliable mathematical models. The pathway and rate-controlling steps of the adsorption process are shown by kinetic models, such as the pseudo-first-order and pseudo-second-order, which also show whether the process is controlled by chemisorption or diffusion [15].

The adsorption capacity and affinity between the adsorbent and adsorbate are quantified by use of isotherm models, such as Freundlich (which describes multilayer adsorption on a heterogeneous surface) and Langmuir (which assumes monolayer adsorption on a homogeneous surface) [16]. Thermodynamic analysis exposes the spontaneity, exothermic or endothermic nature, and degree of unpredictability changes during adsorption using metrics like Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$). These factors are essential for scaling up the process [17].

By creating and characterizing a novel activated carbon from the invasive *Eichhornia crassipes* (water hyacinth) and assessing its effectiveness for the sequestration of the antibiotic oxytetracycline from aqueous solutions, this study aims to fill a crucial research gap. Among the particular goals are:

(1) Preparing and characterizing activated carbon from water hyacinth biomass through chemical activation; (2) examining the impact of important operational parameters (initial concentration, adsorbent dose, pH, contact time, and temperature) on OTC adsorption efficiency;

(3) using kinetic, isotherm, and thermodynamic models to analyze the experimental data in order to clarify the adsorption mechanism; and (4) evaluating the material's potential as a sustainable, affordable, and high-performance adsorbent for reducing pharmaceutical pollution in water. By turning an environmental annoyance into a purification tool and advancing the development of sustainable water treatment technologies, this research is in line with the ideas of green chemistry and the circular economy.

Materials and Methods

Sample Collection and Pre-treatment:

Mature water hyacinth (*Eichhornia crassipes*) was collected from University of Ilorin dam and the biomass were thoroughly washed with tap water to remove silt, debris, and epiphytes, followed by a rinse with distilled water. They were oven dried at 105°C for 24 hours until a constant weight was achieved. The dried biomass was grinded into a fine powder at <500 µm mesh size using a mechanical crusher.

Carbonization and activation of the sample

The 5 g of the grinded biomass was weighed in a crucible and introduced in to a muffle furnace, where it underwent carbonization in an oxygen-free, isolated atmosphere maintained by inert nitrogen gas at 450°C for two hours. The resulting carbonized material was then crushed using a mortar to complete the process. For the chemical activation stage, the carbonized material was mixed with 0.1 M hydrochloric acid at a ratio of 1.2 ml acid per 1g of carbon. This mixture was returned to the isolated muffle furnace and heated to 800°C for 2 hours to activate the carbon. After activation, the material was removed, allowed to cool, and thoroughly washed with de-ionized water. The washed activated carbon was then air-dried and further dried in an oven at 105°C for three hours. Finally, the finished product was sieved to a particle size range of 0.100-0.200 mm and left at room temperature to prepare it for subsequent adsorption experiments [18]. The adsorbent were divided in to three and were denoted as commercial activated carbon (CAC), water hyacinth activated carbon (WHAC) and water hyacinth unactivated (WHUAC).

Preparation of oxytetracycline solutions

The 1000 ppm of OTC were prepared accordingly by weighing and dissolving 1 g of OTC in 1 litre volumetric flasks and it was made to the mark with more de-ionized water. Other concentrations of 10, 25, 50, 75, 100, 200, and 500 ppm were prepared were prepared from the stock solution by serial dilution [19].

Batch Adsorption Experiments

The adsorption of OTC on WHAC was investigated by batch adsorption experiments. The optimization of adsorption parameters were done and the amount of metal ion adsorbed by the acid modified and activated carbon was calculated by using the following equation

$$Q_e = \frac{(C_o - C_e)V}{W} \qquad (1)$$

Where qe is the equilibrium concentration of the adsorbed OTC uptake capacity (mg/l), Co and Ce are the initial and final concentration of OTC in solution at any time, t (mg/l), V is the total volume of the OTC standard solution in the flask (L), W is the mass of adsorbent used (g) [20].

Effect of initial OTC Concentration

Different concentrations of the adsorbate were prepared: 50, 100, 150, 200, 250, 300, 350, 400,450, and 500 (mg/l) by serial dilution of the stock solution and then contacted with a fixed dosage of the adsorbent of 0.2 g in 100 ml conical flask containing 25 ml of the adsorbate. It was then agitated for 2 hours. At the end of agitation time the mixture were filtered and analyzed using Atomic Adsorption Spectrophotometer [21]

Effect of Contact Time

The effect of contact time on OTC adsorption was studied using OTC concentration that gave optimal adsorption at different time intervals (30, 60, 90, 120, 150, 180, and 210 minutes). A 25 ml of OTC concentration (equilibrium concentration) of the adsorbate were contacted with 0.2 g dosage of the adsorbent, the mixture was shaken for 2 hours. The mixture was filtered and analyzed using Atomic Absorption spectrophotometer [21]

Effect of Adsorbent Dose

The OTC concentration that gave optimal adsorption per 0.2 g was used. A 25 ml of the adsorbate was contacted with varying amounts of the adsorbent doses (0.1, 0.2, 0.3, 0.4, 0.5, and 0.5 g) at the equilibrium concentration (concentration of maximum adsorption). The mixture was agitated with an orbital mechanical shaker for 2 hours. The resultant solution was filtered and the filtrates were analyzed using Atomic Absorption Spectrophotometer (AAS) [21].

Effect of pH

A 25ml of the optimum (equilibrium) concentration for Co (II) ion were contacted with 0.2 g of the adsorbent in a 100 ml conical flask and the pH of the solution matrix was varied with 0.1M HCl and 0.1M NaOH to obtain pH of 2,3,4,5,6,7,8,9,10 and 11. The solution was equilibrated for 2 hours, the resultant mixture was filtered and the residual metal ion concentrations were analyzed using Atomic Absorption Spectrophotometer [21].

Effect of Temperature

The various used temperature are 20, 25, 30, 35, 40, 45, 50, 5, 60, 65 and 70 ^oC. A 25 ml of the optimum concentration for OTC were contacted with 0.2 g of the adsorbent in a 100 ml conical flask. The mixtures were equilibrated for 2 hours at stated temperatures. The resultant mixtures were filtered. The filtrate was analyzed using Atomic Absorption Spectrophotometer [21].

Kinetic study profile

The experimental data were subjected to the kinetics profile such as, pseudo-first and pseudo-second order kinetics model and the equations are stated as follows.

(i) Pseudo-first order kinetics

The rate law is given below:

$$\frac{dq_t}{dt} = k_1(q_{e\,-}\, q_t) \qquad (2)$$

Where, q_e and q_t are the amount of OTC adsorbed at equilibrium and time t, respectively, k_1 is the rate constant for the pseudo first order adsorption. The integrated rate law is given as follows

$$log(q_e - qt) = logq_e - \frac{K}{2.303} \qquad (3)$$

A plot of $log(q_e - q_t)$ against t was made and the values of k_1 and q_e were obtained from the slope and intercept, respectively [22].

(ii) Pseudo-second order kinetics

The linear form of pseudo-second order kinetics model is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (4)$$

Where, q_e and q_t are the amount of OTC adsorbed per unit mass of the adsorbent (in mg g^{-1}) at equilibrium and time *t*, respectively, and k_2 is the pseudo second order rate constant. A linear plot of t/q_t against t confirms the fitness of data to this model [22]

Adsorption Isotherms

Three adsorption isotherms were employed in this study and their respective formula are given below.

(i) Langmuir adsorption isotherm

Langmuir adsorption isotherm equation is given below:

$$\frac{Ce}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} Ce \qquad (5)$$

where *Ce* is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium (mg/g), q_{max} is the maximum amount of adsorption with complete monolayer coverage on the adsorbent surface (mg/g) and K_L is the Langmuir constant (L/mg)

(ii) Freundlich adsorption isotherm

Freundlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \qquad (6)$$

Where q_e is the quantity of solute adsorbed at equilibrium (adsorption density: mg of adsorbate per g of adsorbent). C_e is the concentration of adsorbate at equilibrium, K_f and n are the empirical constants dependent on several factors and n is greater than one [23].

(iii) Temkim isotherm

Temkim isotherm is given by the following equation:

$$Q_e = \frac{RT}{b} \ln K_T C_e \qquad (7)$$

Equation above can be linearized into the following:

$$Q_e = B \ln K_T + B \ln C_e \qquad (8)$$

$$where\ B = \frac{RT}{b}$$

Regression of Q_e against $\ln C_e$ enables the determination of isotherm constant K_T and B. The K_T is the equilibrium binding constant (L/mg) corresponding to maximum binding energy constant and is related to the heat of adsorption.

Thermodynamics Studies

The thermodynamics parameters such as Gibbs free energy change (ΔG), Enthalpy change (ΔH) and Entropy change (ΔS) were also studied in order to understand better the effect of temperature on the adsorption of Co (II) ions. The Gibb's free energy change (ΔG) is related to the thermodynamics equilibrium constant by the following equation:

$$K_c = \frac{C_{A_e}}{C_e} \qquad (9)$$

$$\Delta G^0 = -RT \ln K_c \qquad (10)$$

$$\log K_C = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \qquad (11)$$

Where, K_c is the equilibrium constant, C_e is the equilibrium concentration in solution (mg/L) and C_{Ae} is the solid-phase concentration at equilibrium (mg/L). ΔG, ΔH and ΔS are changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol/K), respectively. R is the molar gas constant (8.314 J/mol/K) and T is the temperature (K). The values of ΔH and ΔS were determined from the slope and the intercept of Van't Hoff plots of log K_c versus 1/T [21].

Results and Discussion

Characterization of Adsorbents

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is an indispensable tool for characterizing activated carbons (ACs), as it provides high-resolution topographical and morphological information crucial for understanding their adsorptive properties. The technique reveals surface characteristics, pore structure, and textural details, which are directly linked to an adsorbent's capacity and efficiency [24]. This analysis presents SEM micrographs for three materials: commercial activated carbon (CAC), water hyacinth-based activated carbon (WHAC), and unactivated water hyacinth (WHUAC) (Figures 1a-c).

The SEM analysis reveals distinct porous structures across the activated samples (CAC and WHAC). Both exhibit surfaces with cavities, recessed regions, and protruding features, indicative of a well-developed pore network. Figure 1b (WHAC) shows a weave-like structure with larger pores, likely resulting from the dehydrating and oxidizing effects of the acid activation agent, which creates channels by removing volatile matter and etching the carbon structure [25]. The "weave-like" structure of Water Hyacinth Activated Carbon is important because it masterfully solves the core challenges of adsorption. It makes the high-surface-area interior accessible, allows for high capacity, and enables fast adsorption kinetics. This natural hierarchical structure, a legacy of the water hyacinth's plant-based origin, is what makes it a highly effective and versatile material for purification and environmental remediation. The morphological similarities between CAC (Figure 1a) and WHAC (Figure 1b) specifically their rough, agglomerated, and porous surfaces suggest that water hyacinth is a viable precursor for producing high-quality activated carbon. In contrast, WHUAC (Figure 1c) exhibits a coarser and less developed pore structure, confirming that the activation process is critical for creating the necessary surface area and porosity [25, 26]

The presence of a heterogeneous and highly porous morphology in WHAC, as evidenced by the SEM micrographs, indicates its strong potential for application in wastewater treatment. The available surface area and pore network are essential for the adsorption of organic and inorganic pollutants, a correlation consistently supported by recent literature [27].

The present study is in line with literatures Yakout *et al*. [24] who characterized AC from water hyacinth using SEM and found a highly porous surface morphology after chemical activation.

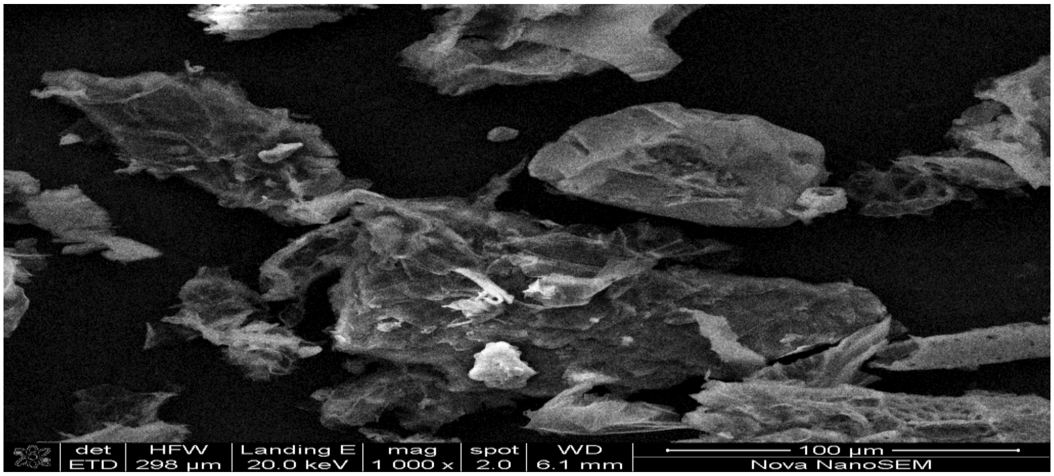

Figure 1a: Commercial activated carbon

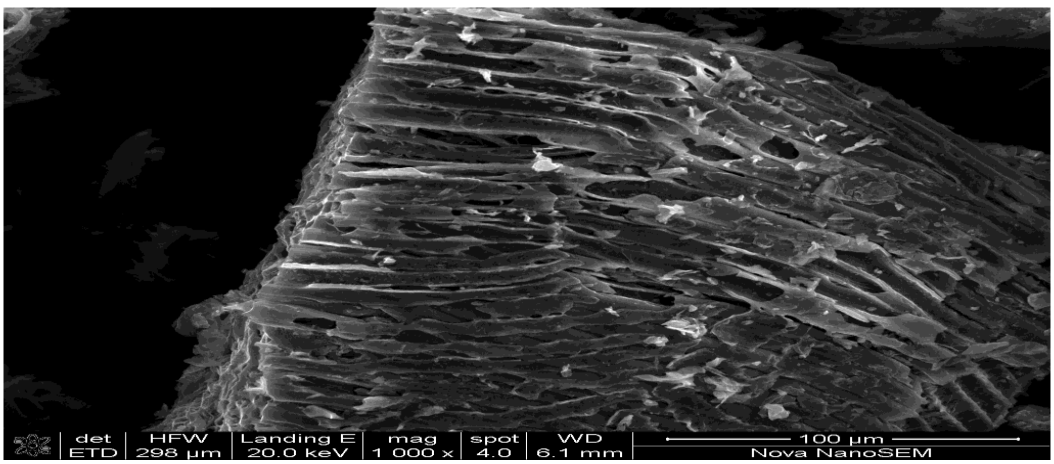

Figure 1b: Water hyacinth activated carbon

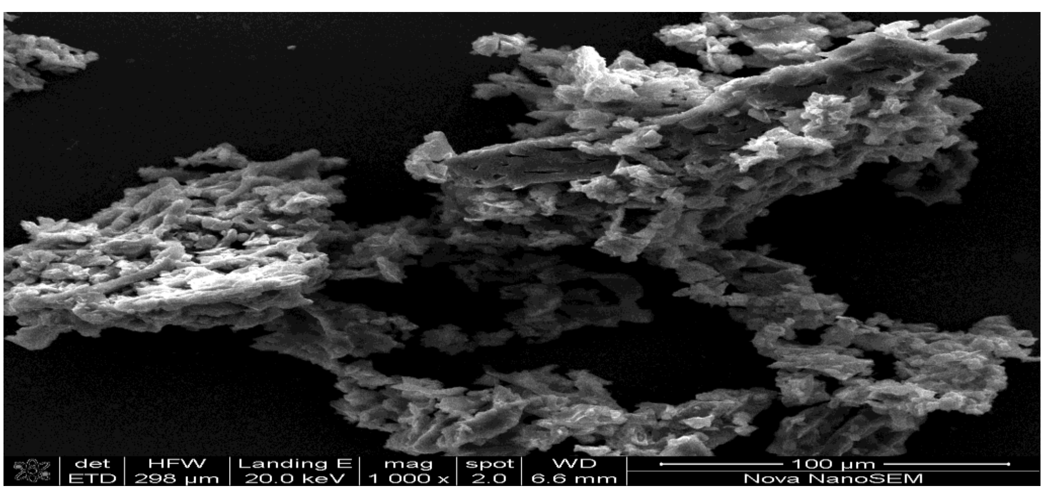

Figure 1c: Water hyacinth unactivated carbon

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier-transform infrared (FTIR) spectroscopy was employed to identify the functional groups and binding sites present on the surfaces of the adsorbents: commercial activated carbon (CAC) and water hyacinth-based activated carbon (WHUAC). The analysis was conducted using a Shimadzu FTIR spectrometer. The resulting spectra (Figure 2) reveal the molecular structure and surface characteristics of the activated carbons.

All samples exhibited a strong, broad absorption band in the region of 3400–3420 cm^{-1}, which is characteristic of O-H stretching vibrations, primarily from hydroxyl groups in cellulose and lignin, as well as from adsorbed water molecules [28]. A band observed near 1400 cm^{-1} is indicative of C–H bending vibrations in methylene or methyl groups [29]. Furthermore, a distinct band at approximately 1590 cm^{-1} corresponds to C=C stretching vibrations in aromatic rings, a key feature of the graphitic structure in activated carbons [30]. The presence of these specific functional groups on the surface of water hyacinth activated carbon (WHAC) is not incidental; it is crucial to its function and performance as an adsorbent**.** The FTIR spectrum confirms that the activation process successfully converted the natural polymers in water hyacinth (cellulose, lignin) into a carbonaceous material with a graphitic-like structure, while retaining and introducing key surface functional groups**.** These groups are directly responsible for the material's adsorptive properties [30].

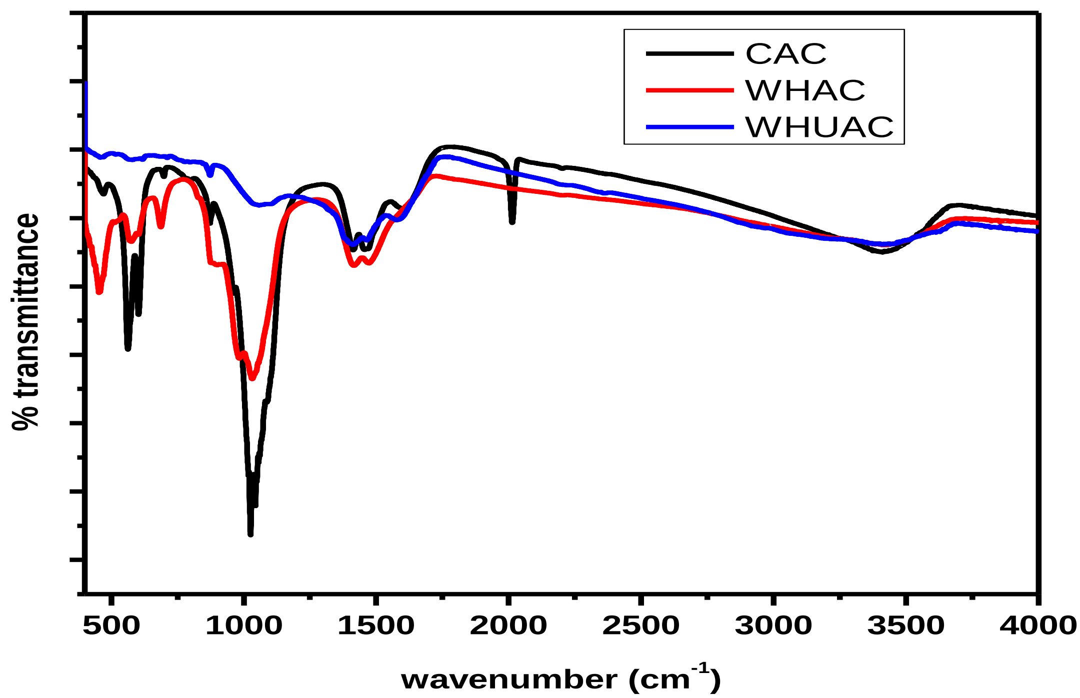

Figure 2: FTIR spectrum of CAC, WHAC and WHUAC

Adsorption Experiment Result

Effect of Initial Concentration

The effect of the initial Oxytetracycline (OTC) concentration on its removal by water hyacinth-based activated carbon (WHAC) was investigated across a range of 50 to 500 mg/L (Figure 3). The results demonstrate that the adsorption capacity (q_e) increased from 12.08 to 115.4 mg/g as the initial OTC concentration rose. This trend is attributed to the driving force provided by a higher concentration gradient, which enhances the diffusion of OTC molecules toward the limited number of available active sites on the adsorbent surface [31]. The findings align with the conclusion of Patel *et al*. [32], who stated that at higher concentrations, the collision frequency between antibiotic molecules and adsorbent sites increases significantly, leading to greater uptake until the surface becomes saturated. The maximum adsorption capacity of WHAC for OTC was 115.4 mg/g**,** achieved at the highest tested initial concentration of 500 mg/L. The maximum capacity of 115.4 mg/g for WHAC is competitive when compared to other green adsorbents developed recently. For instance, a microalgae-based biochar achieved a capacity of 102.7 mg/g for OTC [33], while a modified clay adsorbent showed a capacity of 88.2 mg/g [34]. This positions WHAC as a highly effective material for OTC sequestration, showcasing the success of utilizing water hyacinth as a precursor.

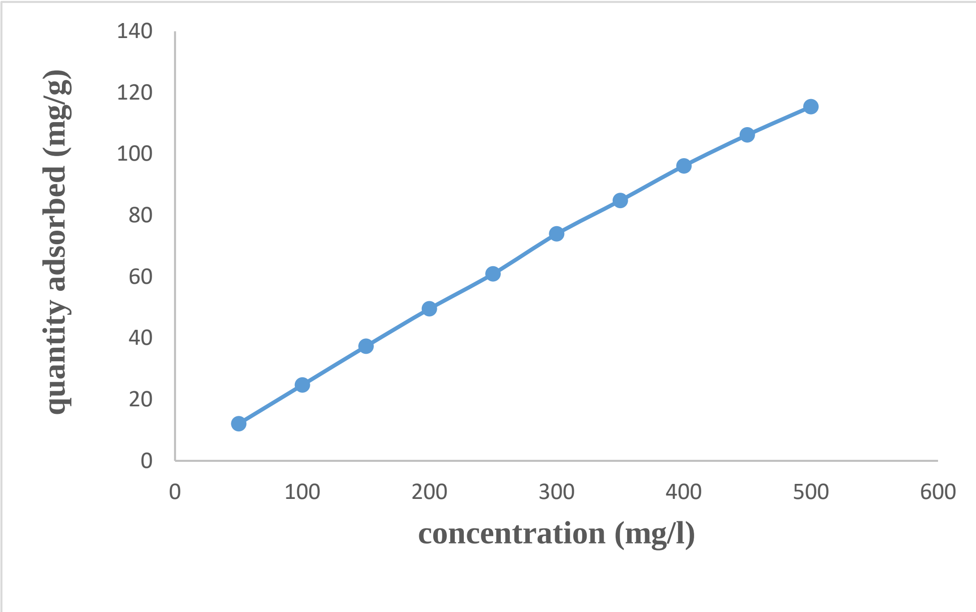

Figure 3: Effect on initial Concentration of OTC onto WHAC

Effect of Adsorbent Dosage

The effect of adsorbent dosage on the removal of oxytetracycline (OTC) was investigated by varying the mass of water hyacinth-based activated carbon (WHAC) from 0.1 g to 0.6 g (Figure 4). The results indicate an inverse relationship between the adsorbent dosage and the adsorption capacity (q_e). Specifically, the quantity of OTC adsorbed per unit mass of WHAC decreased as the dosage increased across the studied range. The factor of particle aggregation and site overlap is strongly supported by the work of [35]. In their study on ciprofloxacin adsorption, they used microscopy to show that higher doses of carbon-based adsorbents led to agglomeration, which effectively blocked pores and reduced the overall accessibility of binding sites.

This observed decrease in adsorption capacity with higher adsorbent mass is a common phenomenon in adsorption studies and can be attributed to site unsaturation [36], and **site overlap/aggregation** [37, 38].

Based on the highest adsorption capacity achieved, the optimum dosage for OTC removal under these experimental conditions was determined to be 0.1 g, yielding a maximum capacity of 60 mg/g**.**

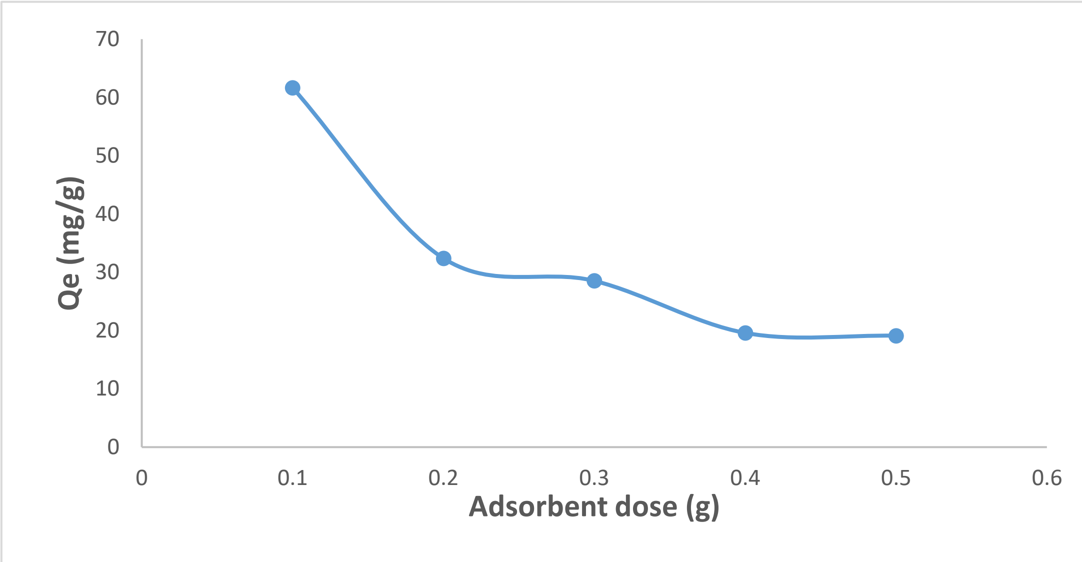

Figure 4: Effect of adsorbent dose on the OTC removal on WHAC

Effect of Contact Time

Contact time is a critical parameter in adsorption studies, as it directly influences the kinetics and equilibrium of the process. To investigate the kinetics of oxytetracycline (OTC) adsorption onto water hyacinth-based activated carbon (WHAC), the contact time was varied from 30 to 210 minutes while keeping other parameters constant. The resulting time profile (Figure 5) reveals that the adsorption capacity increased rapidly in the initial stages before reaching a plateau. The initial high rate of adsorption is attributed to the abundant availability of active sites on the adsorbent surface and a high concentration gradient, which acts as a strong driving force for the diffusion of OTC molecules from the bulk solution to the adsorbent surface. The rate of adsorption markedly decreased after approximately 90 minutes, achieving full equilibrium at 150 minutes with a maximum adsorption capacity of 73.14 mg/g**.** This plateau occurs as the active sites become occupied and the concentration gradient driving the process diminishes. The slight decrease in capacity observed after 150 minutes is likely due to a minor desorption phenomenon, where a small fraction of the weakly bound OTC molecules returns to the solution phase after the system reaches saturation, a behaviour noted in other adsorption studies. A 2023 study on tetracycline adsorption onto sludge-derived biochar reported an almost identical trend, with rapid removal within the first 60 minutes (accounting for ~80% of total uptake) followed by a gradual approach to equilibrium at 120 minutes [39]. The authors also attributed the fast phase to surface diffusion and the slower phase to intra-particle diffusion into narrower pores.

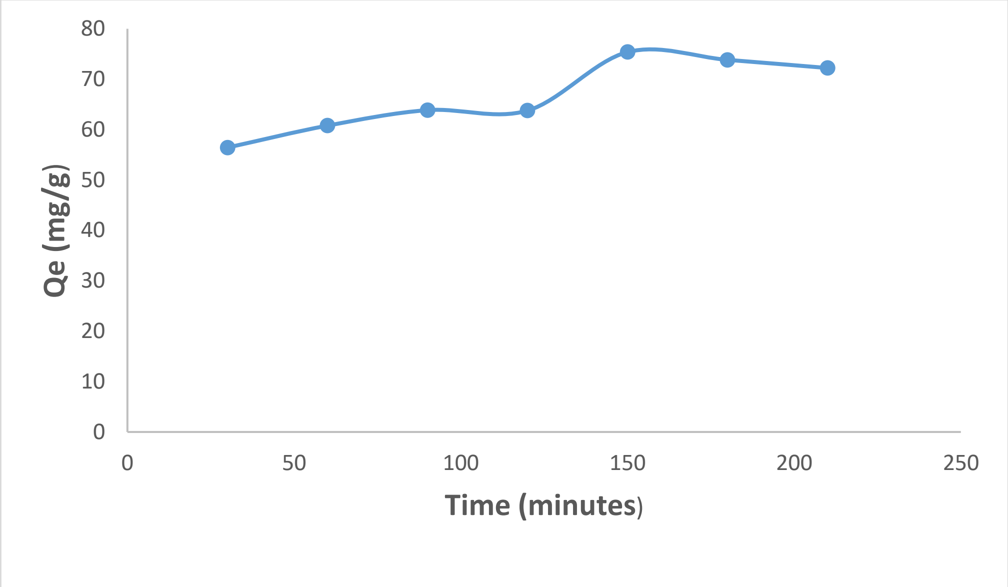

Figure 5: Effect of contact time on OTC removal on WHAC

Effect of pH

The pH of the aqueous solution is a critical operational parameter that significantly influences the adsorption process by altering the surface charge of the adsorbent and the ionization state of the adsorbate. The effect of pH on the adsorption of oxytetracycline (OTC) onto water hyacinth-based activated carbon (WHAC) was investigated across a pH range of 2 to 9.

As illustrated in Figure 6, the adsorption capacity increased sharply from 13.24 mg/g at pH 2 to a maximum of 60.13 mg/g at pH 5. A slight decrease was observed at pH 6 (50.74 mg/g), followed by a gradual increase to 58.33 mg/g at pH 9.

This pH-dependent behaviour can be explained by the electrostatic interactions between the surface charge of WHAC and the ionic species of OTC, which is an amphoteric molecule. At low pH (2-5), the surface of activated carbon typically carries a positive charge in highly acidic conditions due to the protonation of acidic functional groups (e.g., -COOH → $-COOH_2^+$). However, OTC primarily exists as a cation (H_3OTC^+) in this range. The observed increase in adsorption as pH rises from 2 to 5 suggests that mechanisms beyond electrostatic attraction, such as π-π interactions and hydrogen bonding, become more dominant. The initial low adsorption at pH 2 may be due to competitive adsorption between H_3OTC^+ and the high concentration of H^+ ions for the limited active sites. At near-neutral to alkaline pH (6-9), the slight dip at pH 6 coincides with the zwitterionic form of OTC ($H_2OTC^{+/-}$), which may have a lower affinity for the adsorbent surface. As the pH increases further, the WHAC surface becomes increasingly negatively charged, while OTC exists primarily as an anion ($HOTC^-$ and OTC^{2-}). The subsequent increase in adsorption capacity suggests that strong non-electrostatic mechanisms, such as π-π electron donor-acceptor (EDA) interactions, complexation, and pore filling, are the primary drivers for OTC uptake on carbonaceous materials, overcoming any potential electrostatic repulsion. The findings align strongly with the work of Li *et al.* [40], who investigated tetracycline adsorption on soybean straw-derived biochar. [41], in their study on ciprofloxacin removal, noted a similar dip in adsorption capacity at the pH where the zwitterionic form dominated, attributing it to the molecule's neutral net charge reducing its electrostatic interaction potential with the adsorbent surface.

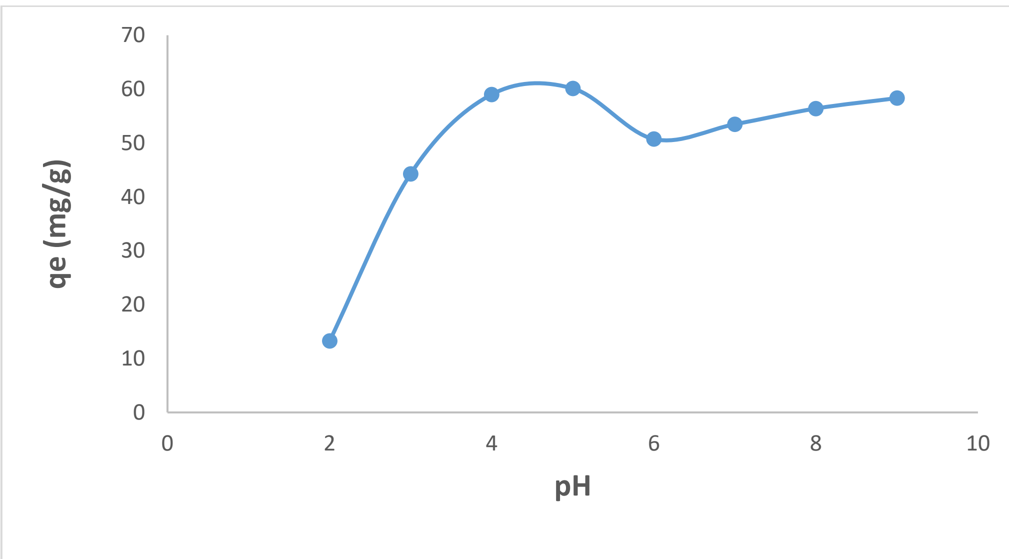

Figure 6: Effect of pH on OTC removal on WHAC

Effect of Temperature

The influence of temperature on the adsorption of oxytetracycline (OTC) onto water hyacinth-based activated carbon (WHAC) was evaluated across a range of 30 to 70 °C (Figure 7). The results indicate that the adsorption capacity (q_e) increased from 30 °C to a maximum of 110.4 mg/g at 60 °C**,** after which it decreased to 80 mg/g at 70 °C.

This temperature-dependent behaviour provides critical insight into the nature of the adsorption process. The initial increase in capacity with rising temperature suggests an endothermic reaction. This endothermicity can be attributed to **e**nhanced molecular mobility **and d**ehydration of Adsorbate and Adsorbent. The decrease in adsorption capacity observed at 70 °C may indicate a point of physical instability for the adsorption complex, where the energy supplied becomes sufficient to overcome the binding forces, leading to increased desorption. The finding that adsorption capacity increases with temperature is consistent with numerous recent studies on antibiotic adsorption. For instance, research by Yadav *et al.* [42] on tetracycline removal using a composite hydrogel adsorbent reported a similar endothermic trend up to 45°C, which they attributed to the increased diffusion rate and the endothermic nature of the pore penetration process. The decline in capacity after an optimum temperature is a critical observation. A recent study by Okoli *et al.* [43] on ciprofloxacin adsorption noted a similar decrease above 50°C.

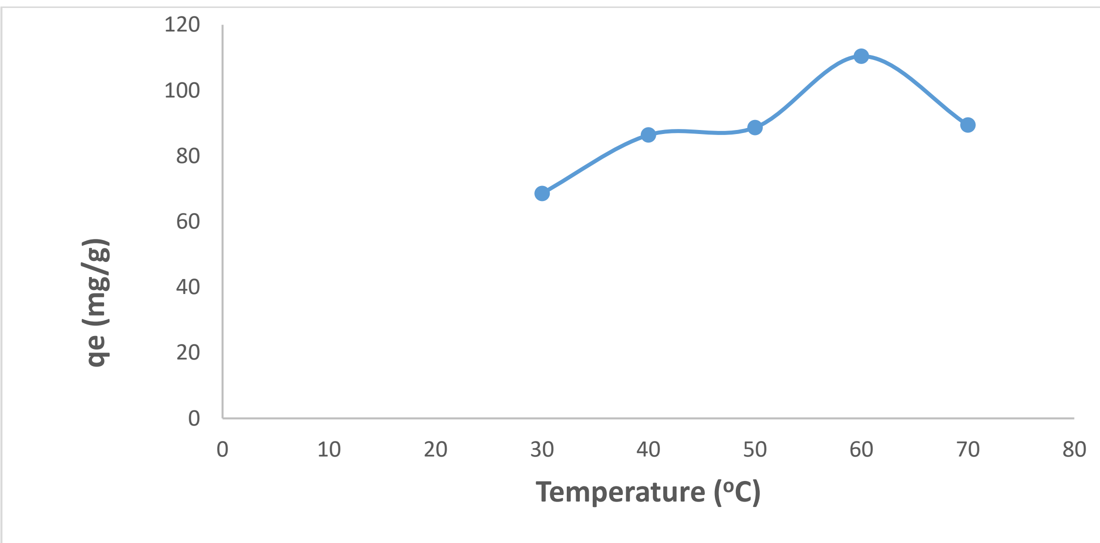

Figure 7: Effect of temperature on OTC on WHAC

Adsorption Isotherms

The experimental equilibrium data were modeled using the Langmuir and Freundlich isotherm theories. The corresponding plots are presented in Figures 8 and 9, and the evaluated parameters for both models are summarized in Table 1. Analysis of the correlation coefficients reveals that the adsorption of WHAC onto OTC is best described by the Langmuir isotherm model (R^2 = 0.99), suggesting a monolayer adsorption mechanism onto a surface with a finite number of identical sites [44]. This finding is consistent with several recent studies on the adsorption of organic compounds, where the Langmuir model provided the best fit for the experimental data [45, 46].

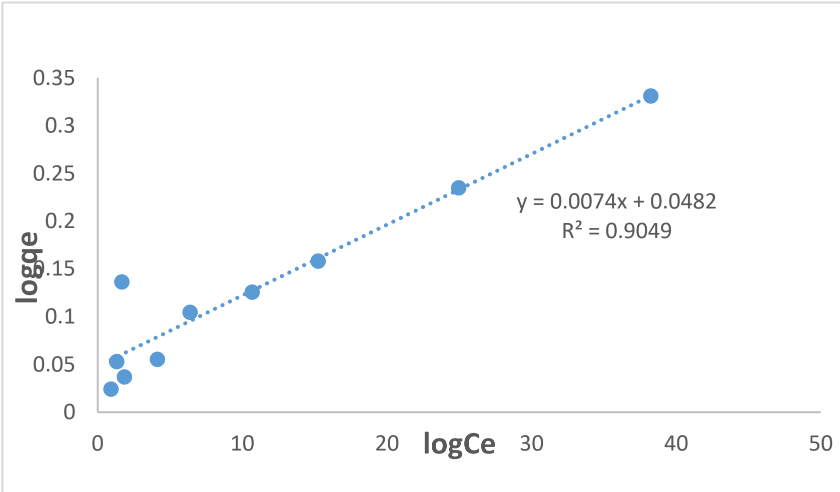

Figure 8: Langmuir adsorption Isotherm plot for OTC on WHAC

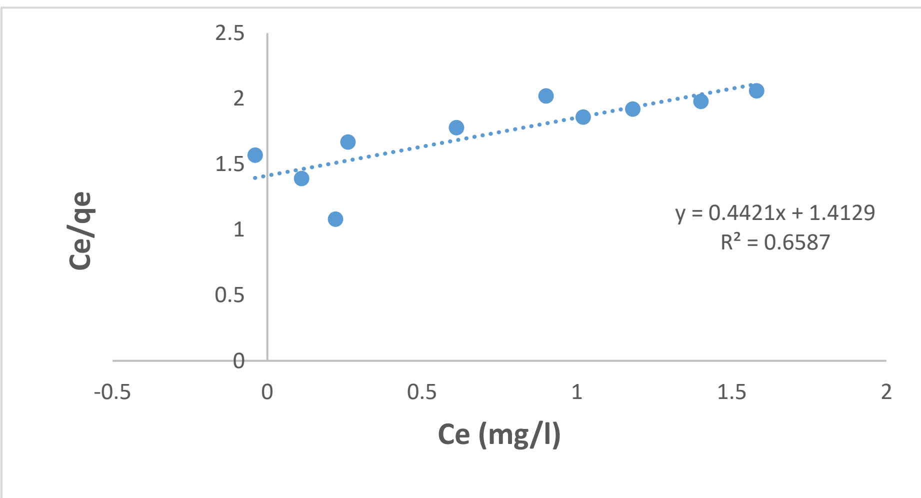

Figure 9: Freundlich adsorption Isotherm plot for OTC on WHAC

Adsorption Kinetics

Kinetics of adsorption is the tool used to examine the rate of the adsorption process, encompassing aspects such as chemical reaction and mass transfer; therefore, a suitable model is needed to analyze the rate data. The pseudo-first-order kinetic model and the pseudo-second-order model are the most frequently used kinetics models in the literature to predict the mechanism involved in the sorption process [47]. These models were applied to test the adsorption kinetics of OTC onto the WHAC adsorbent.

The kinetics model plots are presented in Figures 10-11, and the calculated constants are shown in

Table 2. Comparison of the two models revealed that the adsorption of OTC is best described by the pseudo-second-order model. This conclusion was based on the higher correlation coefficient (R^2) values for the pseudo-second-order model compared to those of the pseudo-first-order model, a finding consistent with previous studies [47, 48]. Recent research on composite adsorbents has further validated the prevalence of pseudo-second-order kinetics in complex adsorption systems [49].

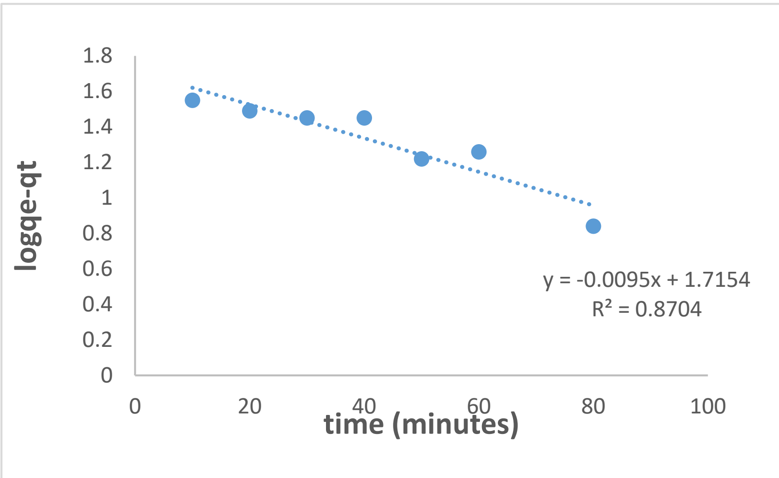

Figure 10: First order kinetics plot for OTC removal on WHAC

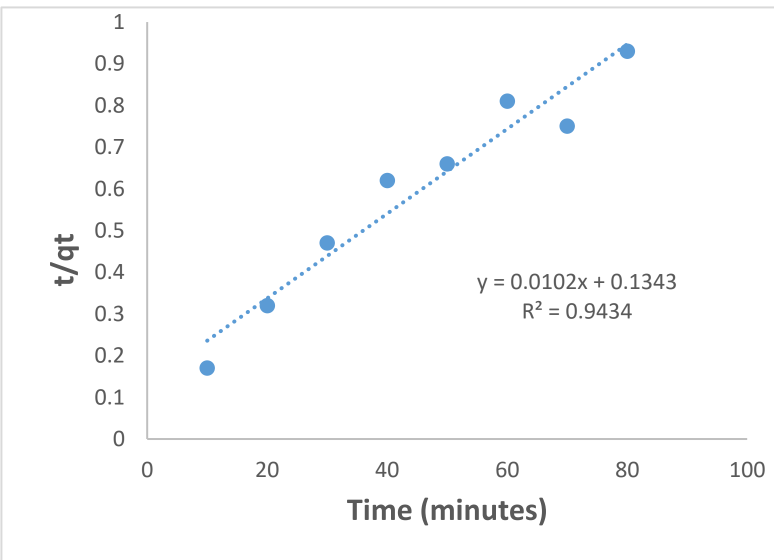

Figure 11: Second order adsorption kinetics for OTC removal onto WHAC

Table 2: Kinetics parameters for OTC adsorption on WHAC

Adsorption kinetics	**Parameters**	
Pseudo-first order	qe	0.022
	K_1	0.8704
	R_2	0.870
Pseudo-second order	qe	98.039
	K_2	$7.75\times^{10\ -4}$
	R^2	0.943

Thermodynamics Studies

The values of enthalpy change (ΔH) and entropy change (ΔS) were obtained from the slopes and intercepts respectively, from the graph of ΔG against T (Figure 12) and respected thermodynamic parameters are shown in Table 3 and it could be observed that Gibb's free energy change (ΔG) were negative while entropy change (ΔS) and enthalpy change (ΔH) was positive in the same way.

The negative values of ΔG decreased with the rise in temperature, indicating that the adsorption of oxytetracycline on the WHAC was feasible and spontaneous [50]. The positive values of ΔH suggested that the OTC adsorption is an endothermic process whereas the positive values of ΔS indicated the increase of randomness at the solid/solution interface adsorption of oxytetracycline on WHAC [50].

Conclusion

This research demonstrates that water hyacinth-activated carbon (WHAC) is a highly effective, sustainable, and economically viable adsorbent for purifying water contaminated with antibiotics like oxytetracycline (OTC). The adsorption process was found to be highly dependent on operational parameters, with optimal removal achieved at pH 5. The system followed the Langmuir isotherm, indicating monolayer adsorption, and a pseudo-second-order kinetic model, suggesting adsorption was governed by chemisorption. With a high maximum capacity of 115.4 mg g^{-1} and a spontaneous, endothermic nature, the process is both efficient and practical. The significant real-world application of this finding lies in creating a circular economy to manage a damaging environmental problem. Communities, particularly in tropical and subtropical regions plagued by water hyacinth invasions, can now harvest this invasive weed and transform it into a valuable resource for local water treatment. This approach simultaneously clears choked waterways, restoring ecosystems and navigation, while providing a low-cost, locally-produced material to treat wastewater from sources like aquaculture, livestock operations, and pharmaceutical effluents where antibiotic pollution is a concern.

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