

Development of Coconut Shell Hydrochar for Lead Removal from Pharmaceutical Wastewater

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Abstract

Lead (Pb^{2+}) contamination of wastewater requires effective, low-cost, and sustainable treatment materials. This study investigated coconut shell hydrochar produced by hydrothermal carbonization (HTC) for Pb^{2+} removal from aqueous solution and pharmaceutical wastewater. Coconut shells were converted to hydrochar at 200, 220, and 240 °C and characterized using proximate, Fourier transform infrared spectroscopy – FTIR, ultimate analysis and BET surface area. The hydrochar produced at 240 °C exhibited a specific surface area of 560.45 m²/g and was selected for adsorption experiments. Batch adsorption studies evaluated the effects of pH, contact time, dosage concentration, temperature, and initial Pb^{2+} concentration. Adsorption equilibrium, kinetics, and thermodynamics were assessed using Langmuir, Freundlich, pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. Pb^{2+} removal increased if contact time and adsorbent dosage increases reaching 99.19% at 120 min and 99.46% at 2.0 g/L, respectively. Increasing initial Pb^{2+} concentration increased adsorption capacity from 0.01665 to 0.180 mg/g but reduced percentage removal. The Freundlich model provided the best equilibrium fit ($R^2 = 0.9996$), while the Langmuir model gave $R^2 = 0.9374$ and a maximum adsorption capacity of 0.2502 mg/g. The pseudo-second-order model best fit the adsorption kinetics ($R^2 = 0.955$). Thermodynamic analysis indicated spontaneous and endothermic adsorption, with negative ΔG values (-0.708 to -2.443 kJ/mol), ΔH of 25.15 kJ/mol, and ΔS of 86.72 J/mol·K. Overall, coconut shell hydrochar showed promising potential for sustainable Pb^{2+} removal from wastewater.

Keywords: Coconut shell hydrochar; Hydrothermal carbonization; Pb^{2+} adsorption; Pharmaceutical wastewater; Heavy-metal removal.

Introduction

The contamination of water resources by heavy metals has become an important environmental concern because of the persistence, toxicity, and potential bioaccumulation of these pollutants. Among the potentially toxic elements, lead (Pb^{2+}) is of particular concern due to its adverse effects on human health and aquatic ecosystems [1]. Pb^{2+} can enter water systems through industrial activities, mining and metallurgical operations, battery manufacturing, pigments, and pharmaceutical and chemical processes. Unlike many organic pollutants, lead cannot be degraded into harmless products and therefore requires effective removal from contaminated water before discharge or reuse [1]. Different treatment approaches have been tried for taking out Pb^{2+} from wastewater including membrane filtration, chemical precipitation, ion exchange, coagulation and adsorption [2]. Although these methods can be effective, some require high operating costs, generate secondary waste, or involve complex treatment processes. Adsorption has become a subject of growing research interest because of its simplicity, effectiveness, ease of operation, and potential for treating low concentrations of heavy metals [2,7]. The development of low-cost and environmentally sustainable adsorbents has further increased the potential application of adsorption for wastewater treatment.

Agricultural residues provide feedstock for the generating low-cost adsorbents because of their availability, renewable, and relatively inexpensive [2]. Coconut shells are suitable on account of their high proportion of lignocellulosic components and carbon and are generated in large quantities as an agricultural waste. Converting coconut-shell waste into hydrochar through hydrothermal carbonization provides an opportunity to produce a value-added adsorbent while simultaneously reducing waste disposal problems [3]. Hydrothermal carbonization is advantageous because it can be undertaken using water and at relatively moderate temperatures, producing a carbon-rich material with active groups on surface that bind metal ions [3, 6].

The adsorption of Pb^{2+} onto hydrochar is influenced by different factors, like solution chemistry, adsorbent characteristics, contact time, temperature, initial metal concentration and the availability of surface-active groups [4, 6, 7]. Isotherm models such as Freundlich and Langmuir are commonly used to describe adsorption equilibrium and to provide information on surface characteristics and adsorption capacity [7]. Similarly, kinetic models help to establish the rate and possible controlling mechanisms of adsorption, while thermodynamic parameters provide information on how spontaneous and heat effects associated alongside the process [7]. Despite the increasing interest in biomass-derived adsorbents, further investigation is required to establish the performance of coconut-shell hydrochar for Pb^{2+} removal under different conditions and, importantly, in real wastewater matrices. Real pharmaceutical wastewater contains a complex mixture of dissolved substances that is in competition with Pb^{2+} for available adsorption sites and consequently influence treatment performance.

Therefore, this study investigated its potential for coconut-shell hydro-char as a low-cost adsorbent for Pb^{2+} clearance from aqueous solution and pharmaceutical wastewater. The study evaluated the effect of initial Pb^{2+} concentration on adsorption performance and determined the equilibrium behaviour using Freundlich and Langmuir isotherm models. The kinetic results were fitted to using pseudo-first-order, pseudo-second-order, and intraparticle diffusion models, while thermodynamic parameters were determined at different temperatures. Finally, the hydrochar was applied to real pharmaceutical wastewater to assess its practical potential for lead removal. The study provides an approach for converting coconut-shell waste into a useful adsorbent while contributing to the development of a simple and sustainable method for heavy-metal removal from wastewater.

2.0. Materials and Methods

2.1 Materials and Reagents

Coconut shell biomasses were obtained from local markets in Minna, Niger State, Nigeria. The shells were separated from the coconut flesh and outer husk, washed repeatedly with tap water to remove soil, organic debris, and loose surface material, rinsed with distilled water, and oven-dried at 105 °C for 24 h. The dried shells were crushed using a hammer mill and sieved to obtain a particle size fraction of 1–2 mm. The prepared biomass was stored in sealed airtight plastic bags until use. Particle size selection was based on previously reported hydrochar and biochar adsorption studies using lignocellulosic biomass [8, 9]. All chemicals used were of analytical reagent grade. Hydrochloric acid (HCl) and sodium hydroxide (NaOH), each prepared at 0.1 mol L⁻¹, were used for pH adjustment. Distilled water was used for solution preparation, washing, and dilution. New solutions were prepared prior to each experiment.

2.2 Collection and Characterization of Pharmaceutical Wastewater

Pharmaceutical wastewater specimens were taken from JESIL Pharmaceutical Industries Ltd., Minna, Niger State, Nigeria. Samples were collected in 1-L high-density polyethylene (HDPE) bottles pre-treated by soaking in 10% HNO_3 for 24 h and rinsing (five times) with distilled water. At the sampling location, each bottle was further rinsed (five times) with the wastewater before collection of the final sample.

Immediately after collection, the samples were acidified to pH 2 using concentrated HNO_3 to inhibit microbial activity and minimize metal precipitation during transportation and storage. The samples were transported to the laboratory in a cool box and stored at 4 °C. Analyses and adsorption experiments involving the real wastewater were commenced within 48 h of collection.

Before adsorption experiments, the raw wastewater was characterized for pH, electrical conductivity and turbidity, total dissolved solids (TDS), and lead concentration. Pb^{2+} concentration was determined by filtering the wastewater through a 0.45- μm membrane filter and analysing the filtrate by flame atomic absorption spectroscopy - FAAS at 283.3 nm. The measured lead concentration was used as the initial concentration (C_0) for the real wastewater adsorption experiment.

2.3 Production of Coconut Shell Hydrochar

Pharmaceutical wastewater samples were gathered from JESIL Pharmaceutical Industries Ltd., Minna, Niger State, Nigeria. Samples were collected in 1-L high-density polyethylene (HDPE) bottles pre-treated by soaking in 10% HNO_3 for 24 h and rinsing (three times) with distilled water. At the sampling location, each bottle was further rinsed (three times) with the wastewater before collection of the final sample.

Immediately after collection, the samples were acidified to pH 2 using concentrated HNO_3 to inhibit microbial activity and minimize metal precipitation during storage and transportation. The samples were transported to the laboratory in a cool box and stored at 4 °C. Analyses and adsorption experiments involving the real wastewater were commenced within 48 h of collection.

Before adsorption experiments, the raw wastewater was characterized for physicochemical properties pH, turbidity, electrical conductivity, total dissolved solids (TDS), and lead concentration. Pb^{2+} concentration was determined by filtering the wastewater through a 0.45- μm membrane filter and analysing the filtrate by flame

atomic absorption spectroscopy - FAAS at 283.3 nm. The measured lead concentration was used as the initial concentration (C_0) for the real wastewater adsorption experiment.

2.3 Production of Coconut Shell Hydrochar

Coconut shell hydrochar was produced by hydrothermal carbonization (HTC). The Teflon liner of the autoclave was washed with 10% NaOH and placed in an oven at 100 °C for 20 min before use. A 60-g portion of dried shell was mixed with 300 mL of distilled water in a 500-mL Teflon-lined stainless-steel autoclave, giving a biomass-to-water ratio of 1:5 (w/v). Similar hydrothermal treatment approaches have been used for the preparation of biomass-derived hydrochars for heavy-metal adsorption [10, 11].

The autoclave was tightly sealed and placed in a muffle furnace preheated to the target temperature. Hydrothermal carbonization was conducted at 200, 220, and 240 °C for a fixed residence time of 2 h. These temperatures were selected to investigate the impact of HTC temperature on the surface properties and adsorption performance of the resulting hydrochars. Earlier studies have shown that hydrothermal or thermal treatment conditions can affect the surface characteristics, functional groups, pore structure, and adsorption performance of biomass-derived carbon materials [12–14].

Following the 2-h residence period, the autoclave was allowed to cool naturally to room temperature. The solid hydrochar was separated from the process liquid by vacuum filtration using Whatman No. 3 filter paper. The recovered hydrochar was many times washed with distilled water until the filtrate became clear and then dried at 110 °C for 2 h. Hydro-char yield was calculated as:

$$\text{Hydrochar yield (\%)} = \frac{\text{mass of dried hydrochar}}{\text{mass of dry coconut shell}} \times 100 \quad (1)$$

The dried hydrochars were stored in sealed glass vials labelled according to their production temperature. The hydrochar exhibiting the most suitable combination of surface area, functional-group density, and yield was selected for subsequent adsorption experiments. The selection of an optimized hydrochar based on its physicochemical properties and Pb(II) adsorption performance is consistent with approaches reported for biomass-derived hydrochars [13].

2.4 Characterization of Coconut Shell Hydrochar

The physicochemical and surface properties of the raw coconut shell and produced hydrochars were determined to assess the effect of HTC temperature and identify the most suitable material for lead adsorption. Similar characterization tools have been applied to biomass-derived carbon materials used for Pb(II) adsorption [8, 11, 12, 13].

2.4.1 Proximate and Ultimate Analysis

Proximate analysis was carry-out to determine moisture, ash, volatile matter, and fixed carbon contents of the raw coconut shell and produced hydrochars according to ASTM D3173, D3174, and D3175. Ultimate analysis was conducted using a CHNS/O elemental analyzer to determine the carbon, hydrogen, nitrogen, sulfur, and oxygen contents, with oxygen calculated by difference.

2.4.2 BET Surface Area and Porosity Analysis

The textural properties including total pore volume, surface area and average pore diameter of the hydrochar samples were determined using the Brunauer–Emmett–Teller (BET) method based on nitrogen adsorption–desorption analysis. Dried hydrochar was loaded into a 9-mm sample cell and prepared for BET analysis according to the instrument procedure. Surface area and pore characteristics are important properties when assessing the adsorption behaviour of biomass-derived carbon materials [9, 10, 13].

2.4.3 Fourier Transform Infrared Spectroscopy - FTIR

FTIR - spectroscopy was used to find the surface-active groups present on the raw coconut shell and hydrochar surfaces. The spectra were used to assess changes in surface functional groups resulting from HTC and to identify functional groups potentially involved in lead adsorption. FTIR analysis has been extensively employed to examine changes in surface functional groups associated with Pb(II) adsorption onto biomass-derived hydrochars and biochars [10, 12, 14].

2.5 Batch Adsorption Tests

Batch adsorption tests were conducted to investigate the effects of solution Ph , contact time, adsorbent dosage,, starting lead concentration and temperature on lead adsorption by the selected coconut shell hydrochar.

These variables are commonly investigated when assessing the adsorption performance of biomass-derived materials for Pb(II) removal [8–10].

Unless otherwise stated, experiments were conducted in 100-mL Erlenmeyer flasks containing 50 mL of lead solution and agitated at 150 rpm. Following each experiment, the suspension was obtained through a 0.45- μ m membrane filter and the residual Pb²⁺ concentration was determined by FAAS at 283.3 nm.

Blank controls containing lead solution without hydrochar were included to account for non-adsorptive lead losses. All glassware was acid-washed with 10% HNO₃ and rinsed three times (3) with distilled water before use.

The Pb²⁺ removal efficiency (%) and equilibrium adsorption capacity were determined using the following Equations (2) and (3):

$$\text{Lead removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (3)$$

where C_0 and C_e are the starting and equilibrium lead concentrations (mg L⁻¹), respectively, V - is the solution volume (L), and m is the mass of hydrochar (g).

2.5.1 Effect of Solution pH

Lead adsorption was examined at different solution pH values over the range of pH 4–8. Each flask contained 50 mL of 50 mg L⁻¹ lead solution, adjusted to the desired pH using 0.1 mol L⁻¹ HCl or NaOH. Hydrochar was added at a dosage of 1.0 g L⁻¹, corresponding to 0.05 g per flask. Contact time, temperature, and shaking speed were maintained at 120 min, 25 °C, and 150 rpm, respectively. The investigation of solution pH is important because protonation/deprotonation of surface functional groups and the compound form of Pb(II) in solution can influence adsorption performance [1, 3, 7].

The pH was measured before hydrochar addition, after addition, and at the end of the experiment. The pH producing the highest Pb²⁺ removal was selected as the optimum pH for subsequent experiments.

2.5.2 Effect of Contact Time

The effect of reaction duration was investigated using 50 mL of 50 mg L⁻¹ lead solution adjusted to the optimum pH. Hydrochar was added at a dosage of 0.05 g per flask. The suspensions were agitated at 150 rpm, and samples were withdrawn at 30, 60, 90, and 120 min. Each sample was without delay filtered and analysed for residual lead concentration. A blank flask without hydrochar was maintained for 120 min to verify lead stability during the experimental period.

The equilibrium contact time was identified as the point at which no further significant increase in adsorption capacity occurred. The resulting data were used for kinetic modelling. Contact-time experiments and kinetic modelling have been used extensively to evaluate the adsorption rate of Pb(II) onto biomass-derived carbon materials [8], [9], [13].

2.5.3 Effect of Adsorbent Dosage

The effect of hydrochar dosage was investigated at four dosage levels: 0.5, 1.0, 1.5 and 2.0 g L⁻¹, corresponding to hydrochar masses of 0.050, 0.100, 0.150, and 0.200 g, respectively, in 50 mL of lead solution. The experiments were conducted at the optimum pH and equilibrium contact time, with temperature maintained at 25 °C. A blank control containing lead solution without hydrochar was included. The optimum dosage was selected based on lead removal efficiency and adsorption capacity. The impact of adsorbent dosage on Pb(II) removal has been reported for different biomass-derived adsorbents [13].

2.5.4 Effect of Initial Pb(II) Concentration

The effect of initial Pb²⁺ concentration was investigated to obtain equilibrium adsorption data for Langmuir and Freundlich isotherm modelling. This experiment was conducted using several initial lead concentrations while maintaining the optimum pH, hydrochar dosage, equilibrium contact time, and temperature constant. For each initial concentration, 50 mL of lead solution was contacted with the selected hydrochar under the optimized conditions. After equilibrium, the suspensions were filtered through 0.45- μ m membrane filters and the remaining Pb(II) concentration (C_e) was determined by FAAS.

The equilibrium adsorption capacity (q_e) was calculated for each concentration run using:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (4)$$

The resulting C_e and q_e values were used to construct the adsorption isotherm and fit the Langmuir and Freundlich models. These models have been applied to evaluate equilibrium adsorption behaviour and Pb(II) uptake by biomass-derived carbon materials [14].

2.5.5 Effect of Temperature

The effect of temperature was investigated at 25, 35, and 45 °C to provide data for thermodynamic analysis. Flasks containing 50 mg L⁻¹ lead solution at the optimum pH and optimum hydrochar dosage were pre-equilibrated at the target temperature in a thermostated water bath for 15 min before shaking. The suspensions were then agitated at the 150 rpm for the equilibrium contact time. A blank control without hydrochar was maintained at 45 °C to assess potential non-adsorptive changes in lead concentration at the highest experimental temperature.

Temperature-dependent adsorption studies have been used to assess the influence of temperature on Pb(II) uptake and to obtain thermodynamic parameters for biomass-derived adsorbents [8, 13].

2.6 Adsorption Isotherm Modelling

The equilibrium data obtained from the initial Pb²⁺ concentration experiment were fitted to the Langmuir and Freundlich adsorption isotherm models. The use of these models allows assessment of equilibrium adsorption behaviour and estimation of adsorption capacity and surface heterogeneity. Both models have been used to describe Pb(II) adsorption onto biochars and hydrochars derived from different biomass sources [1, 2, 6, 7].

2.6.1 Langmuir Isotherm

The Langmuir model describes monolayer adsorption on a relatively identical adsorption sites adsorption sites. The linearized Langmuir equation was expressed as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_L} \quad (5)$$

where q_{max} is the maximum theoretical monolayer adsorption capacity (mg g⁻¹), K_L is the Langmuir equilibrium constant (L mg⁻¹), C_e is the equilibrium lead concentration (mg L⁻¹), and q_e is the equilibrium adsorption capacity (mg g⁻¹). The dimensionless separation factor was calculated using:

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

An R_L value ranging between 0 to 1 suggests that adsorption is favourable, while values above 1 indicate an unfavourable adsorption process.

2.6.2 Freundlich Isotherm

The Freundlich model is an empirical model used to describe adsorption on heterogeneous surfaces with a non-uniform distribution of adsorption energies. Its linearized form was expressed as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

where K_F is the Freundlich adsorption capacity constant and $1/n$ is the heterogeneity factor. A value of $1/n < 1$ indicates favourable adsorption. The values of K_F and $1/n$ were obtained from the intercept and slope, respectively, of a plot of $\log q_e$ against $\log C_e$. The better-fitting model was selected based on the coefficient of determination (R^2) and agreement between calculated and experimental adsorption capacities.

2.7 Adsorption Kinetic Modelling

The kinetic data obtained from the contact-time experiment were fitted to pseudo-first-order, pseudo-second-order, and intraparticle diffusion models to determine the rate and possible controlling mechanism of Pb²⁺ adsorption onto the coconut shell hydrochar. These models are widely adopted to examine adsorption kinetics and possible mass-transfer limitations in Pb(II) adsorption studies [13, 14].

2.7.1 Pseudo-First-Order Model

The linearized pseudo-first-order equation was expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (8)$$

where q_t is the adsorption capacity at different time t - (mg g^{-1}), q_e is the equilibrium adsorption uptake (mg g^{-1}), and k_1 is the pseudo-first-order rate constant (min^{-1}).

2.7.2 Pseudo-Second-Order Model

The linearized pseudo-second-order model was expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

where k_2 is the pseudo-second-order rate constant. The values of q_e and k_2 were determined from the slope and the intercept of a plot of t/q against t . The model with the higher R^2 and closer agreement between calculated and experimental q_e was considered the better descriptor of the adsorption kinetics.

2.9 Analytical Methods

Lead concentrations in filtered samples were determined using flame atomic absorption spectroscopy (FAAS) at 283.3 nm. Calibration standards were made from a certified lead reference standard. Samples exceeding the calibration range were diluted by a known factor before analysis, and the measured concentrations were corrected using the dilution factor.

For samples with relatively low lead concentrations, an appropriate lower calibration range was used. Solution pH was measured using a calibrated bench-top digital pH meter, while turbidity, electrical conductivity, and TDS were determined using calibrated meters.

2.10 Quality Assurance and Data Analysis

All batch adsorption experiments were conducted in duplicate, and mean values were reported. Where the relative standard deviation between duplicate measurements exceeded 5%, the experiment was repeated.

Blank control experiments without hydrochar were conducted alongside the adsorption experiments to account for non-adsorptive lead losses. Where the blank showed a decrease exceeding 2% of the initial lead concentration, the corresponding loss was used to correct the measured equilibrium concentrations.

Isotherm and kinetic parameters were obtained by linear regression of the respective linearized equations. The goodness of fit was evaluated using the coefficient of determination (R^2), together with comparison between calculated and experimentally measured equilibrium adsorption capacities.

4.0 Results and Discussion

4.1 Proximate and Ultimate Composition of Coconut Shell and Hydrochar

The proximate and ultimate compositions of the raw coconut shell and hydrochars produced at 200, 220, and 240 °C are presented in Table 1. Hydrothermal carbonization (HTC) produced clear changes in the physicochemical composition of the biomass, with increasing temperature generally promoting carbon enrichment and reducing volatile and oxygen-containing components.

Table 1: Proximate and ultimate composition of raw coconut shell and hydrochar produced at different HTC temperatures

Sample	Moisture content (%)	Ash content (%)	Fixed carbon (%)	Carbon (%)	Volatile matter (%)	Nitrogen (%)	Hydrogen (%)	Oxygen (%)	O/C
Raw coconut shell	8.54	1.53	14.97	49.33	75.07	0.32	6.31	48.21	0.76
Hydrochar/200 °C	2.97	3.72	44.66	64.14	48.75	0.44	4.52	35.23	0.35
Hydrochar/220 °C	2.53	4.46	50.87	68.17	42.23	0.53	4.16	29.34	0.33
Hydrochar/240 °C	2.17	5.85	54.36	72.16	37.73	0.66	3.96	23.13	0.26

The moisture content decreased from 8.51% in the raw coconut shell to 2.19% in the hydrochar produced at 240 °C, while volatile matter decreased from 75.01 to 37.70%. In contrast, fixed carbon increased from 14.98% in the raw biomass to 54.31% at 240 °C. These changes indicate progressive conversion of the volatile and oxygen-rich components of the lignocellulosic biomass into a more carbon-rich and thermally stable solid during HTC. The observed decrease in volatile matter and increase in fixed carbon with increasing HTC temperature are

consistent with the behaviour reported for hydrochars derived from lignocellulosic biomass [15-19]. The ash content increased from 1.50% in the raw coconut shell to 5.80% at 240 °C. This apparent enrichment in ash is attributable primarily to the loss of organic matter during HTC rather than to the generation of new inorganic material. Consequently, the remaining mineral fraction constitutes a larger proportion of the hydrochar mass as the HTC temperature increases.

The ultimate analysis further demonstrates the progressive carbonization of the coconut shell. Carbon content increased from 49.30% in the raw coconut shell to 72.10% in the 240 °C hydrochar, whereas oxygen decreased from 48.20 to 23.10%. Hydrogen also decreased slightly from 6.30 to 3.92%. The corresponding atomic O/C ratio declined from 0.75 to 0.22, indicating substantial deoxygenation during HTC. Such changes are generally associated with dehydration and decarboxylation reactions, which progressively remove oxygen-containing moieties from the biomass as HTC severity increases (Wang *et al.*, 2025). The reduction in O/C ratio is particularly relevant to the intended application of the hydrochar as a lead adsorbent. Although oxygen-containing functional groups, particularly carboxyl and hydroxyl groups, can provide important sites for Pb²⁺ binding, adsorption performance is determined by the combined effects of surface chemistry, porosity, surface area, and mineral composition rather than by O/C alone (Chen *et al.*, 2024; Malool *et al.*, 2021). Therefore, the lower O/C ratio of the 240 °C hydrochar does not, by itself, establish superior or inferior Pb²⁺ adsorption performance. The BET and FTIR results are considered together with the adsorption results to determine the most suitable HTC temperature [15], [16].

4.2 Hydrochar Yield

The hydrochar yields obtained from coconut shell at the three HTC temperatures are presented in Table 2. A clear decrease in hydro-char yield was observed as the HTC temperature increased from 200 to 240 °C.

Table 2: Hydrochar yield at different hydrothermal carbonization temperatures

HTC run	Biomass	HTC temperature (°C)	Yield (%)
1	Coconut shell	200	80.47
2	Coconut shell	220	62.80
3	Coconut shell	240	57.78

The hydro-char yield decreased from 80.47% at 200 °C to 62.80% at 220 °C and 57.78% at 240 °C, corresponding to an overall reduction of approximately 28% relative to the yield at 200 °C. The progressive reduction in yield indicates increasing conversion of the original biomass into soluble and gaseous products as HTC severity increased.

At higher temperatures, hydrolysis, dehydration, decarboxylation, and fragmentation reactions become more pronounced, resulting in greater transfer of organic components from the solid state into the aqueous state and, to a lesser extent, the gaseous phase. Consequently, less solid hydrochar remains at the end of the process. The observed decrease in yield is therefore consistent with the increased carbonization and deoxygenation reflected in the proximate and ultimate analyses.

The yield results also demonstrate an important trade-off in selecting the HTC temperature. The 200 °C treatment produced the highest hydrochar yield (80.47%), whereas increasing the temperature to 240 °C resulted in a lower yield but produced a hydrochar with substantially higher fixed-carbon and carbon contents and lower O/C ratio (Table 1). Thus, HTC temperature should not be selected solely on the basis of hydrochar yield. The optimum condition should instead be determined by considering hydrochar yield together with surface area, pore characteristics, functional groups, and Pb²⁺ adsorption performance [20], [22].

4.3 Hydrochar Characterization

4.3.1 BET Surface Area and Pore Characteristics

The surface area and pore characteristics of the coconut-shell hydrochar produced at 240 °C were evaluated using nitrogen adsorption-desorption analysis. The corresponding adsorption-desorption isotherm is presented in Figure 1. The hydrochar exhibited a specific surface area of 560.45 m² g⁻¹, indicating the development of a substantial accessible surface during hydrothermal carbonization. Such a surface provides potential sites for interaction with dissolved Pb²⁺ ions and may facilitate adsorption through surface and pore-associated mechanisms.

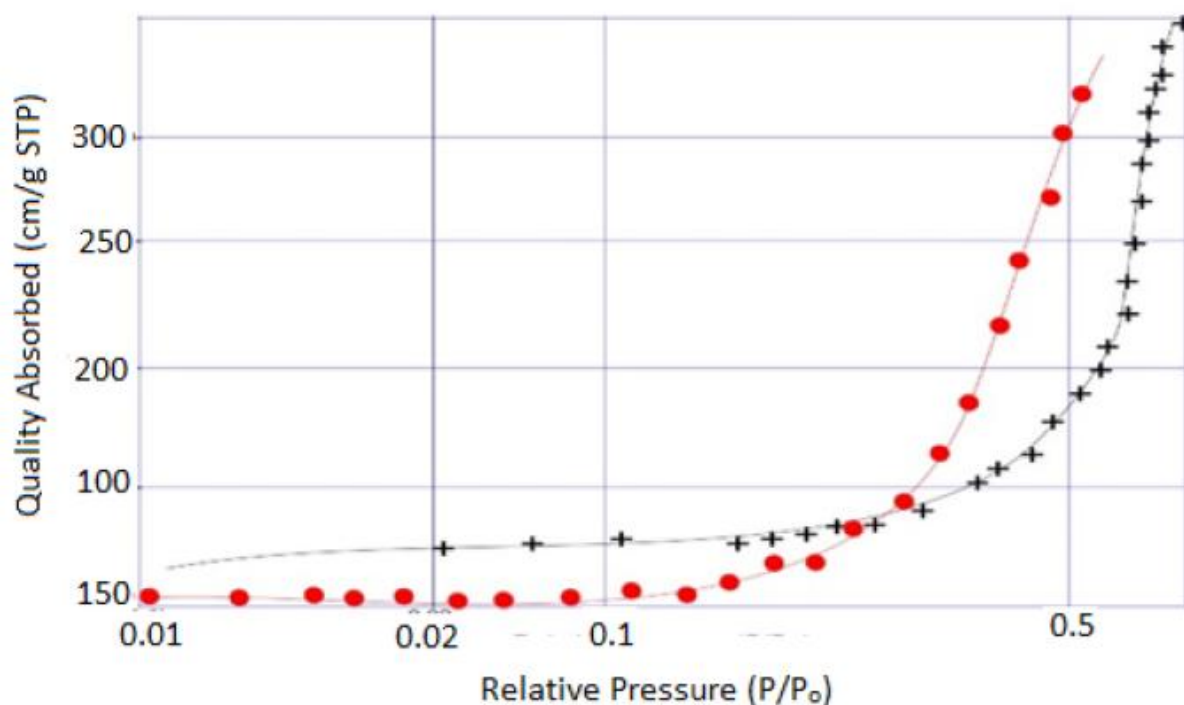


Figure 2. Nitrogen adsorption–desorption isotherm of the coconut-shell hydrochar produced at 240 °C

The BET analysis further gave a t-plot micropore area of 20.40 m² g⁻¹ with external surface area of 22.24 m² g⁻¹. The BJH analysis indicated a cumulative pore volume of approximately 0.523 cm³ g⁻¹. The relatively large external surface area and pore volume suggest that the hydrochar possesses a developed porous structure capable of providing accessible adsorption regions.

The average pore width obtained from the BET analysis was approximately 27.54 Å (2.75 nm), while the BJH adsorption average pore width was 27.26 Å (2.73 nm). These values fall within the mesopore range (2–50 nm), indicating that mesopores constitute an important component of the pore structure. The presence of mesopores can be advantageous for adsorption because they offer accessible pathways for dissolved Pb²⁺ ions can diffuse into the adsorbent and access internal adsorption sites [15], 21, 23, 24].

The adsorption–desorption behaviour shown in Figure 2 is consistent with the presence of a developed porous structure. However, the enhanced BET surface area (850 m²/g) observed should not be interpreted as the sole determinant of lead adsorption performance. Adsorption is also governed by the chemical characteristics of the hydrochar surface, including oxygen-containing functional groups and other active sites capable of interacting with Pb²⁺. Therefore, the BET results should be interpreted together with the FTIR results and subsequent Pb²⁺ adsorption experiments.

4.3.2 Fourier Transform Infrared Spectroscopy Analysis

FTIR - spectroscopy was used to identify the principal surface-active functional groups of the coconut-shell hydrochars and to assess changes in surface active chemistry with increasing hydrothermal carbonization (HTC) temperature. The spectra of the hydrochars produced at 200, 220 and 240 °C are presented in Figure 2.

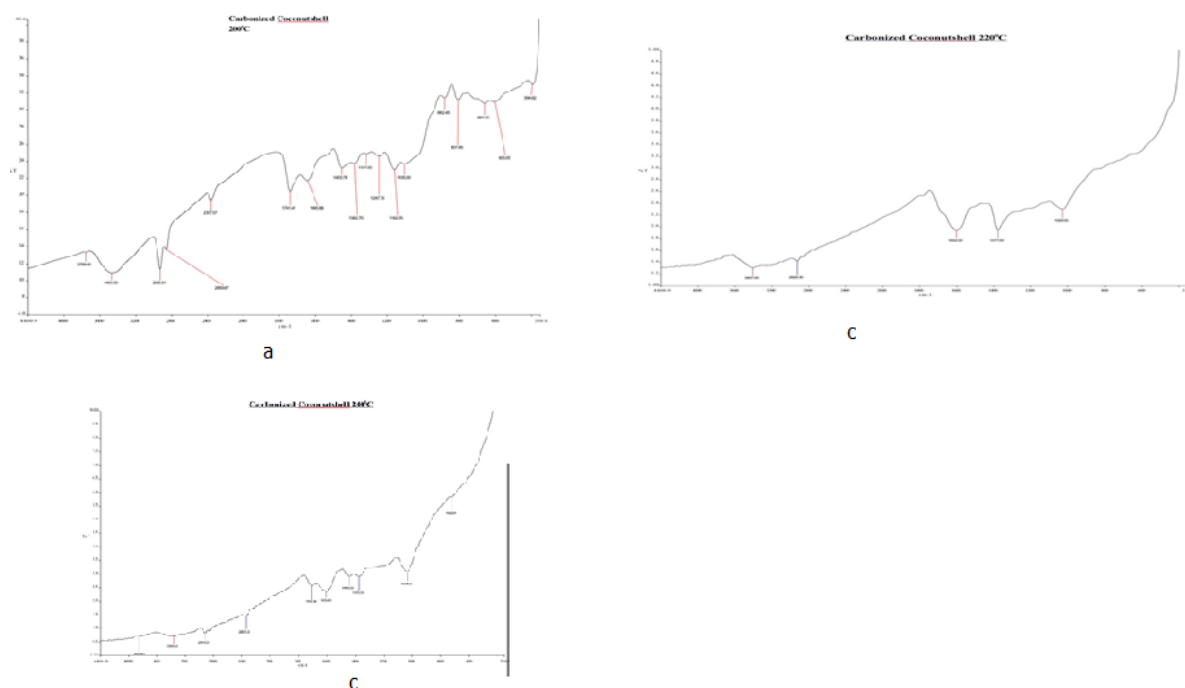


Figure 2. FTIR spectra of coconut-shell hydrochar produced at (a) 200 °C, (b) 220 °C, and (c) 240 °C

The hydrochar produced at 200 °C showed absorption bands at approximately 3463, 2925.81, 2859.67, 1741.41, 1645.66, 1453.78, 1382.70, 1317, 1247.76, 1162.25, and 1105 cm^{-1} . The broad band at 3463 cm^{-1} is associated with O–H stretching, while the bands at 2925.81 and 2859.67 cm^{-1} correspond to aliphatic C–H stretching. The band at 1741.41 cm^{-1} indicates carbonyl (C=O) groups, while bands in the fingerprint region are related to various oxygen-containing and carbonaceous functionalities.

At 220 °C, the major bands occurred at approximately 3407, 2925.30, 1602, 1377, and 1029 cm^{-1} . At 240 °C, bands were observed at approximately 3368, 2919, 1709.38, 1605, 1443, 1375.54, and 1034 cm^{-1} . The progressive changes in band intensity and position, together with the reduction in the number of prominent bands, indicate transformation of some of the original biomass functional groups as HTC temperature increased. Nevertheless, hydroxyl-, carbonyl-, and C–O-related functionalities remained detectable even at 240 °C.

These observations concur with the ultimate analysis, which showed a decrease in oxygen content and O/C ratio with increasing HTC temperature. The persistence of oxygen-containing functional groups is relevant to Pb^{2+} adsorption because such groups can yield potential sites for adsorption of metal ions [15, 21,24].

Overall, the FTIR results confirm that HTC modified the surface chemistry of the coconut shell while retaining potentially active oxygen-containing functionalities. Together with enhanced BET surface area and developed pore structure, these characteristics support the potential of the hydrochar as an adsorbent for Pb^{2+} removal from pharmaceutical wastewater.

4.4 Effect of Contact Time on Lead Removal

The effect of contact time on lead adsorption by coconut shell hydrochar is presented in Table 3 and Figure 3. The experiments were carry-out using real pharmaceutical wastewater at an initial Pb concentration of 0.370 mg/ L, adsorbent dosage of 1 g/L, initial pH of 5.0, and temperature of 25 °C. As shown in Figure 3, Pb removal increased rapidly during the initial contact period and subsequently approached a plateau. The percentage removal rose from 98.11% at 30 min to 98.65% at 60 min, 98.92% at 90 min, and 99.19% at 120 min. Similarly, the adsorption capacity rose slightly from 0.363 to 0.367 mg/g over the same period.

The rapid initial removal observed in Figure 3 can be ascribed to the availability of numerous vacant adsorption sites on the hydrochar and the strong concentration gradient between Pb^{2+} in the solution and the adsorbent surface. These conditions favour rapid transfer of Pb^{2+} ions from the wastewater to the available surface sites. As contact time increased, the accessible adsorption sites became progressively occupied and the concentration gradient decreased, resulting in a slower rate of Pb uptake [22], [23].

Table 3: Effect of Contact Time on Pb(II) Removal by Coconut Shell Hydrochar

Sample Code	Contact Time (min)	Initial pH	Final pH	C ₀ (mg/L)	C _t (mg/L)	q _t (mg/g)	Removal (%)
PA13	30	5.00	6.90	0.375	0.007	0.363	98.11
PA14	60	5.00	6.80	0.375	0.005	0.365	98.65
PA15	90	5.00	6.80	0.375	0.004	0.366	98.92
PA16	120	5.00	7.00	0.375	0.003	0.367	99.19
Blank (PA1)	120	5.00	6.10	—	—	—	—

The relatively flat portion of the curve after 30 min implies that the adsorption process was approaching equilibrium. The increase in removal from 30 to 120 min was only 1.08 percentage points, while the adsorption capacity increased by just 0.004 mg/g. This negligible change suggests that most of the available Pb²⁺ had been eliminated during the initial stage of adsorption, with the remaining uptake occurring more gradually as less accessible sites became involved. The contact time of 120 min was therefore selected as the equilibrium or near-equilibrium contact time for subsequent experiments. Although much of the Pb(II) was removed within the first 30 min, the contact time was extended to 120 min to allow the adsorption process to proceed before the measurements were made.

Overall, Table 3 demonstrates that coconut shell hydrochar provides rapid and highly effective Pb removal, achieving more than 98% removal within 30 min and approximately 99% removal at 120 min. This rapid adsorption behaviour indicates good potential for the hydrochar in practical pharmaceutical wastewater treatment applications.

4.5 Effect of Adsorbent Dosage on Lead Removal

The influence of adsorbent loading on lead removal by coconut shell hydrochar is presented in Table 4 and Figure 4. The adsorption experiments were conducted using real pharmaceutical wastewater with a measured initial Pb concentration ((C₀)) of 0.370 mg/L, contact time of 120 min, temperature of 25 °C, and initial pH of 5.0.

As shown in Figure 4, Pb removal increased with increasing hydrochar dosage, from 98.38% at 0.5 g/L to 99.46% at 2.0 g/L. The increase in removal can be assigned to the greater number of available adsorption sites and increased adsorbent surface area at higher hydrochar dosages. Consequently, more Pb²⁺ ions could interact with the surface-active functional groups of the hydrochar, resulting in a higher fraction of Pb being removed from the wastewater.

However, the improvement in removal became relatively small at higher dosages. Increasing the dosage from 1.0 to 2.0 g/L increased Pb removal from 98.65% to 99.46%, representing an improvement of only 0.81 percentage points. This indicates that most of the available Pb²⁺ ions had already been removed at 1.0 g/L, leaving only a small residual concentration for further adsorption.

In contrast, the adsorption capacity ((q_e)) decreased considerably with increasing dosage, from 0.728 mg/g at 0.5 g/L to 0.184 mg/g at 2.0 g/L. This behaviour occurs because the relatively small amount of Pb present in the solution is distributed over an increasing mass of hydrochar. Thus, although increasing the dosage improves the overall percentage removal, the amount of Pb adsorbed per unit mass of hydrochar decreases. This inverse relationship between adsorbent dosage and adsorption capacity is commonly observed in adsorption systems.

From a practical perspective, 1.0 g/L was selected as the optimum dosage for subsequent experiments. At this dosage, the hydrochar achieved 98.65% Pb removal, reducing the measured Pb concentration from 0.370 to 0.005 mg/L. This represents a high removal efficiency while using less adsorbent than the higher dosages investigated. Increasing the dosage to 1.5 and 2.0 g/L resulted in only marginal improvements in Pb removal, while the adsorption capacity decreased substantially.

Overall, Figure 3 demonstrates that increasing hydrochar dosage improves Pb removal, but the improvement becomes progressively smaller at higher dosages. Considering the high removal efficiency achieved and the lower adsorbent requirement, 1.0 g/L was considered an appropriate operating dosage and was therefore adopted for the subsequent adsorption experiments [21], [23].

Table 4: Effect of Adsorbent Dosage on Pb(II) Removal by Coconut Shell Hydrochar

Sample Code	Hydrochar Mass (g)	Dosage (g/L)	Initial Ph	Final pH	C ₀ (mg/L)	C _e (mg/L)	Removal (%)	q _e (mg/g)
PA-9	0.023	0.6	5.50	4.50	0.375	0.007	98.39	0.729
PA-10	0.053	1.1	5.50	4.70	0.375	0.004	98.66	0.367
PA-11	0.074	1.6	5.50	3.80	0.375	0.004	99.18	0.247
PA-12	0.106	2.1	5.50	4.50	0.375	0.003	99.47	0.186

Blank	-	—	—	5.50	5.90	—	—
PA2	—	—	—	—	—	—	—

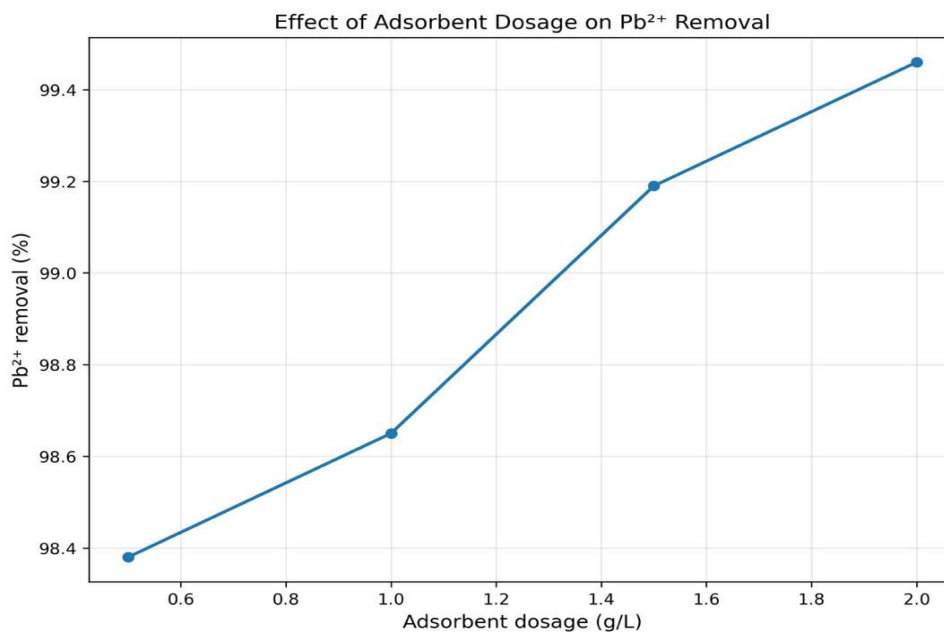


Figure 3. Effect of Coconut Shell Hydrochar Dosage on Pb(II) Removal

4.6 Effect of Temperature on Lead Removal

The impact of temperature on Pb(II) adsorption by coconut shell hydrochar is presented in Table 5 and Figure 5. The experiments were conducted using real pharmaceutical wastewater with a measured initial Pb concentration (C_0) of 0.375 mg/L, contact time of 120 min, adsorbent dosage of 1 g/L, and initial pH of 5.0.

Table 5: Effect of Temperature on Pb(II) Removal by Coconut Shell Hydrochar

Sample Code	Temperature (°C)	Initial pH	Final pH	C_0 (mg/L)	C_e (mg/L)	Removal (%)	q_e (mg/g)
PA17	25	5.00	5.80	0.370	0.011	97.02	0.359
PA18	35	5.00	5.80	0.370	0.009	97.57	0.361
PA19	45	5.00	5.50	0.370	0.006	98.38	0.364
Blank (PA0)	45	5.00	5.80	—	—	—	—

As shown in Figure 4, Pb removal efficiency increased progressively with temperature, from 97.02% at 25 °C to 98.38% at 45 °C. The corresponding adsorption capacity also increased slightly from 0.359 to 0.364 mg/g. This gradual improvement suggests that increasing temperature enhanced the interaction between Pb²⁺ ions and the hydrochar surface. The increase in Pb removal with temperature may be associated with improved diffusion of Pb²⁺ ions through the solution and towards the active sites of the hydrochar. Higher temperature can increase the mobility of Pb²⁺ ions and facilitate their interaction with surface functional groups. The observed increase in adsorption capacity further supports the favourable effect of temperature on the adsorption process under the conditions investigated.

However, the improvement in removal was relatively small, increasing by only 1.36 percentage **points** between 25 and 45 °C. This indicates that temperature had a less pronounced effect on Pb removal compared with parameters such as contact time and adsorbent dosage. Nevertheless, the consistent increase in removal shown in Figure 4 suggests that the adsorption process was favoured by the increase in temperature within the investigated range.

The highest removal of 98.38% was obtained at 45 °C, with a residual Pb concentration **of** 0.006 mg/L. Although the higher temperature improved Pb removal, the relatively modest increase compared with 25 °C indicates that substantial removal can also be achieved at near-ambient conditions. Therefore, temperature

selection for practical application should consider both adsorption performance and the additional energy requirement associated with heating the wastewater.

Based on the results, 45 °C was selected as the optimum temperature within the range investigated, as it produced the highest Pb removal and adsorption capacity. This condition was therefore considered for subsequent adsorption studies.

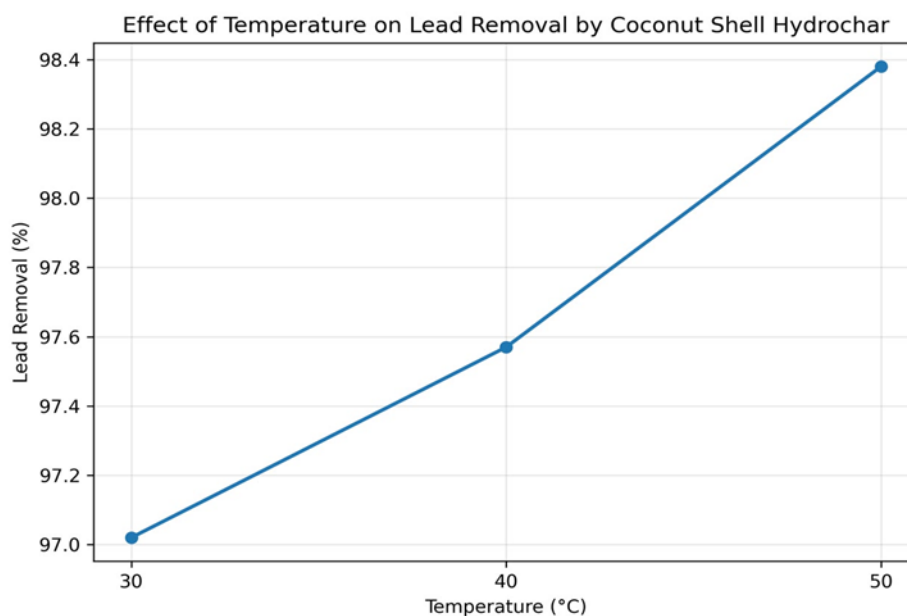


Figure 4: Effect of Temperature on Pb(II) Removal by Coconut Shell Hydrochar

4.7 Effect of Initial Lead Concentration and Adsorption Isotherm Modelling

The effect of initial lead concentration on the adsorption performance of coconut shell hydrochar is presented in Figure 6. At equilibrium, the data recorded at initial Pb concentrations were used to evaluate the adsorption behaviour using the Freundlich and Langmuir isotherm models.

As shown in Figure 6, the percentage removal of Pb decreased as the initial Pb concentration increased, whereas the equilibrium adsorption capacity (q_e) increased. The adsorption capacity increased from 0.01665 mg/g at 0.37 mg/L to 0.180 mg/g at 5.0 mg/L. This increase can be attributed to the greater concentration gradient between the solution and the hydrochar surface at higher Pb concentrations, which enhanced the driving force for the transfer of Pb^{2+} ions to the available active adsorption sites [16, 17, 21].

The decrease in percentage removal at higher concentrations can be explained by the limited number of available adsorption sites on the hydrochar. At lower Pb concentrations, a larger proportion of the Pb^{2+} ions could interact with the available surface sites. As the initial concentration increased, more Pb^{2+} ions competed for the available sites, resulting in a lower percentage removal. Thus, the increase in q_e and decrease in percentage removal indicate progressive loading of Pb onto the hydrochar surface.

The equilibrium parameters used for the isotherm analysis are presented in Table 4.7. The Langmuir model was evaluated using the relationship between C_e/q_e and C_e , while the Freundlich model was evaluated using $\log q_e$ against $\log C_e$.

4.8 Langmuir Isotherm

The linearized Langmuir plot produced a good linear relationship, with an R^2 value of 0.9374. The calculated Langmuir parameters are presented in Table 6. The adsorption maximum monolayer capacity (q_{max}) was 0.2502 mg/g, while the Langmuir constant (K_L) was 1.4433 L/mg.

The relatively high R^2 value indicates that the Langmuir model provided a good representation of the equilibrium data. The model assumes adsorption onto a finite number of relatively uniform sites, resulting in monolayer coverage of the adsorbate. However, its fit was lower than that obtained with the Freundlich model.

The Langmuir separation factor (R_L) ranged from approximately 0.46 to 0.15 across the initial Pb concentration range studied. Since the values were between 0 and 1, the adsorption was considered favourable. The reduction in R_L with increasing initial Pb concentration further indicates that adsorption became more favourable at higher concentrations.

The obtained q_{max} of 0.2502 mg/g represents the estimated maximum adsorption capacity of the hydrochar under the experimental conditions used. Differences from reported capacities of other carbon-based adsorbents

may result from variations in feedstock, hydrothermal carbonization conditions, surface chemistry, activation and the concentration range investigated [17, 23].

4.9 Freundlich Isotherm

The Freundlich model showed an excellent linear relationship, with an R^2 value of 0.9996, as presented in the corresponding isotherm plot. The Freundlich parameters are given in Table 6. The Freundlich capacity constant (K_F) was 0.6576, while the heterogeneity factor ($1/n$) was 1.5208.

The higher R^2 value of the Freundlich model compared with the Langmuir model indicates that it provided a better description of the experimental equilibrium data. This result suggests that Pb^{2+} adsorption occurred predominantly on a heterogeneous hydrochar surface containing adsorption active sites with different energies and affinities. Such behaviour is expected because hydrochar contains different surface functional groups and adsorption sites formed during hydrothermal carbonization.

It should be noted that the calculated $1/n$ value of 1.5208 is greater than 1. Therefore, the criterion of $1/n < 1$ should not be used to describe favourable adsorption for these data. Instead, the Langmuir R_L values provide the appropriate indication of adsorption favourability, while the high Freundlich R^2 value indicates a better fit of the model to the experimental equilibrium data.

Overall, the Freundlich model ($R^2 = 0.9996$) provided a better fit than the Langmuir model ($R^2 = 0.9374$), indicating that surface heterogeneity played an important role in Pb^{2+} adsorption onto the coconut shell hydrochar. Nevertheless, the good Langmuir fit and favourable R_L values show that monolayer adsorption also contributed to the overall adsorption process. As illustrated in Figure 5, increasing the initial Pb concentration increased the amount of Pb adsorbed per unit mass of hydrochar but reduced the percentage removal.

Table 6: Equilibrium Adsorption Data at Different Initial Lead Concentrations

C_0 (mg/L)	C_e (mg/L)	q_e (mg/g)	C_e/q_e	$\text{Log } C_e$	$\text{Log } q_e$
0.37	0.037	0.01665	2.222	-1.432	-1.779
0.50	0.060	0.02200	2.727	-1.222	-1.658
1.00	0.150	0.04250	3.529	-0.824	-1.372
2.00	0.400	0.08000	5.000	-0.398	-1.097
3.00	0.720	0.11400	6.316	-0.143	-0.943
4.00	1.040	0.14800	7.027	0.017	-0.830
5.00	1.400	0.18000	7.778	0.146	-0.745

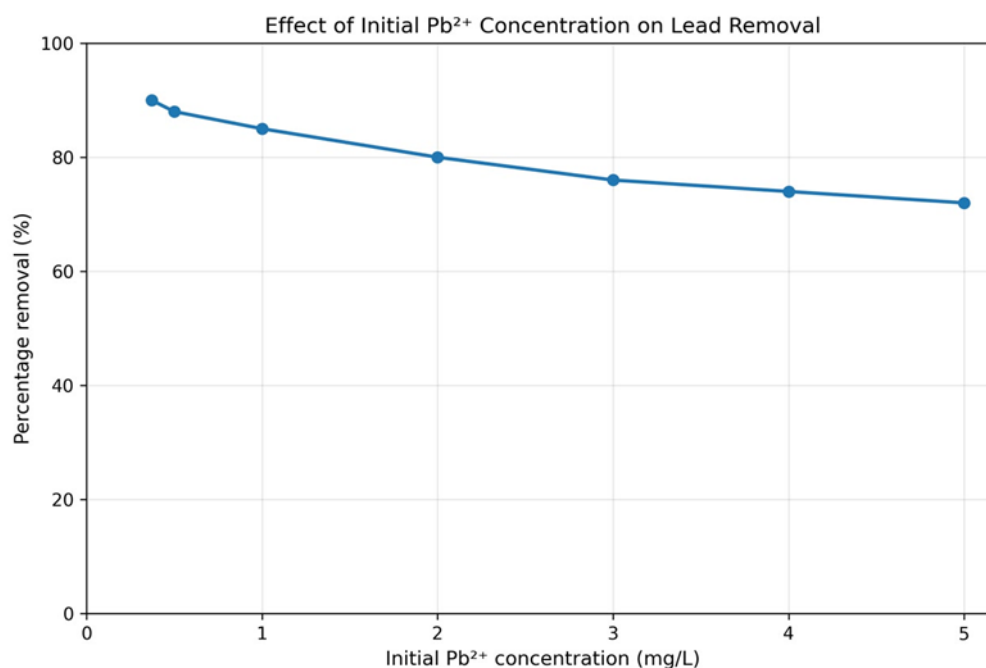


Figure 5: Effect of Initial Lead Concentration on Pb^{2+} Removal and Adsorption Capacity of Coconut Shell Hydrochar

4.11 Adsorption Isotherm Modelling

The equilibrium adsorption data were analysed using the Freundlich and Langmuir isotherm models. The calculated parameters are presented in Table 7. The Langmuir model gave an (R^2) value of 0.9374, with a maximum

adsorption capacity ($q_{\max}$) of **0.2502** mg/g and (K_L) of 1.4433 L/mg. The separation factor (R_L) ranged from 0.1454 to 0.4597, indicating favourable adsorption because the values were between 0 and 1.

The Freundlich model produced a higher (R^2) value of 0.9996, indicating a better fit to the experimental data. The calculated (K_F) was 0.1442, while ($1/n$) was 0.6576 and ($n = 1.5208$). Since ($1/n$) was less than 1 and (n) was greater than 1, the adsorption was favourable and the hydrochar surface exhibited heterogeneous adsorption characteristics.

Table 7: Langmuir and Freundlich Isotherm Parameters for Pb^{2+} Adsorption

Isotherm Model	Parameter	Value
Langmuir	($q_{\max}$) (mg/g)	0.2502
	(K_L) (L/mg)	1.4433
	(R_L)	0.1454–0.4597
	(R^2)	0.9374
Freundlich	(K_F)	0.1442
	($1/n$)	0.6576
	(n)	1.5208
	(R^2)	0.9996

Overall, the Freundlich model provided the better representation of the equilibrium data, suggesting that Pb^{2+} adsorption occurred mainly on a heterogeneous hydrochar surface with adsorption sites of different affinities. The good Langmuir fit and favourable (R_L) values also indicate that monolayer adsorption contributed to the overall process [16, 20, 22].

4.11 Adsorption Kinetic Modelling

The adsorption kinetic data had been fitted to the pseudo-first-order, pseudo-second-order and intraparticle-diffusion models. The results are presented in Table 8.

Table 8: Kinetic Model Parameters for Pb^{2+} Adsorption

Model	Parameter	Value
Pseudo-first-order	(q_e) (mg/g)	0.018
	(k_1) (min^{-1})	0.78
Pseudo-second-order	(q_e) (mg/g)	0.018
	(k_2) ($\text{g/mg} \cdot \text{min}$)	0.039
Intraparticle diffusion	(k_{id}) ($\text{mg/g} \cdot \text{min}^{0.5}$)	0.356
	(C) (mg/g)	0.002
Experimental (q_e)		0.018

The kinetic data were better described by the pseudo-second-order model than the pseudo-first-order model, with R^2 values of 0.955 and 0.935, respectively. The calculated (q_e) also agreed with the experimental value of 0.018 mg/g. This indicates that the pseudo-second-order model described the adsorption kinetics more effectively and suggests that interactions between Pb^{2+} ions and active sites contributed to the adsorption rate.

The intraparticle diffusion model also gave an (R^2) of 0.955, but the non-zero intercept ($C = 0.002$) mg/g). This implies that intraparticle diffusion was not the only rate-limiting mechanism.

4.11 Physicochemical Properties of Pharmaceutical Wastewater

The physicochemical characteristics of the pharmaceutical wastewater before and after treatment are summarized in Table 8. The full results for all individual samples can be retained in the Appendix to avoid making the main chapter unnecessarily long.

Table 8: Summary of Physicochemical Properties of Pharmaceutical Wastewater

Parameter	Raw Wastewater	Range After Treatment
pH	6.00	3.90–7.00
Electrical conductivity ($\mu\text{S/cm}$)	1216	1474–2210
TDS (mg/L)	157	176–315

The raw pharmaceutical wastewater had a pH of 6.00, electrical conductivity of 1216 $\mu\text{S/cm}$ and TDS of 157 mg/L. Following treatment, the pH varied between 3.90 and 7.00, while electrical conductivity and TDS generally

increased. These changes indicate that interaction between the wastewater and hydrochar altered the physicochemical characteristics of the wastewater.

5.0 Conclusion

Coconut shell hydrochar showed good potential as a low-cost and sustainable material for removing Pb^{2+} from wastewater. Hydrothermal carbonization improved the carbon characteristics of the coconut shell, while Pb^{2+} adsorption was affected by contact time, adsorbent dosage, operating temperature, and initial concentration. The adsorption behaviour suggests a heterogeneous, spontaneous, and endothermic process. Overall, the study demonstrates that coconut shell waste can be converted into a useful adsorbent, providing a practical approach to both agricultural waste utilization and heavy-metal wastewater treatment.

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