Cassava Chaff Ash as Potential Adsorbent for Arsenic Ions Removal from Aqueous Solution: Evaluations of Isotherms, Kinetics, and Thermodynamic Properties

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Cassava chaff in its raw and heat-treated (ash) forms was studied as an adsorbent for the removal of arsenic (As(V)) from aqueous solutions in a batch process. The findings indicated that pH significantly influenced As adsorption efficiency on raw cassava chaff, with optimal adsorption (78.6%) observed at a pH of approximately 4.5. Adsorption isotherm modeling revealed that the Langmuir model was more applicable to heat-treated cassava chaff, with maximum adsorption capacity of 101 mg/g, whereas the Freundlich model better described As adsorption on raw cassava chaff with maximum adsorption capacity of 82.2 mg/g. Kinetic studies showed that the pseudo-second-order model accurately represented As adsorption onto raw cassava chaff, while the pseudo-first-order model best fit the kinetics for heat-treated cassava chaff. The enthalpy change for heat-treated cassava chaff and raw sample were +35.3 kJ/mol and +55.3 kJ/mol, respectively, suggesting the process to be endothermic. Information from Fourier transform infrared analysis revealed that the adsorbent was made up of cellulose and hemicellulose materials. Functional groups including OH, C=C, C=O, and C-O may be involved in the uptake of As(V) ions. This work highlights heat-treated cassava chaff as a promising, robust solution for As-contaminated water treatment.

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INTRODUCTION

Water pollution poses significant problems, affecting both human health and ecosystems. A key issue is the contamination of water by harmful substances including chemicals, pharmaceuticals, and heavy metals, often resulting from industrial waste, agricultural runoff, and untreated sewage (Ademoyegun *et al*. 2022). Several critical consequences are associated with water pollution, such as human health issues (cancer, damage to kidney, liver, reproductive and neurological systems) (Lin *et al*. 2022), and ecosystem degradation (disruption of aquatic ecosystems and causing toxic algae blooms, oxygen depletion, and mass die-offs of aquatic life) (Adeogun *et al.* 2018; Ogundiran *et al*. 2022). Addressing water pollution requires international cooperation to improve wastewater treatment, reduce industrial discharge, and implement better agricultural practices. The need for clean water is especially pressing, as climate change exacerbates the problem by increasing the frequency of extreme weather events, further stressing water resources. Conventional methods of removing heavy metals, such as chemical precipitation, ion exchange, and membrane filtration, are often expensive and energy-intensive, which limits their usage (Sahmoune 2018a; Almomani *et al.* 2019; Olaoye *et al*. 2020). However, adsorption has been proposed as a cost-effective method that is reliable in the treatment of wastewater, using activated carbon as the adsorbent. Conventional adsorption methods, such as those using activated carbon, face several challenges, including high costs associated with its usage due to high purity. The high cost makes them less feasible in developing regions (Olaoye *et al*. 2020). Activated carbon is expensive to produce due to energy-intensive processes such as pyrolysis, activation (with steam, chemicals, or heat), and post-treatment. This cost makes the technology less accessible to low-income communities and small-scale water treatment projects and not feasible in developing regions such as Nigeria. Many developing regions lack the infrastructure or technology to produce activated carbon locally, leading to reliance on expensive alternatives. Cassava chaff is a byproduct of cassava processing. It is widely produced in many developing regions, and it’s found in abundance and low cost. This combination makes it an attractive feedstock for adsorbent production. The energy requirements in the conversion of cassava chaff into ash are significantly lower than for activated carbon production, as it involves a straightforward process of heat treatment, which can be done using locally available resources.

The increasing prevalence of arsenic (As) contamination in groundwater and surface water has emerged as a significant global health and environmental concern. Arsenic can be introduced into water bodies through both natural processes and human activities. Typical examples of natural sources are geological formations (occurrence in certain rocks and soils), volcanic activities, hydrothermal activities (like hot springs), and also human activities, such as mining and smelting operations, the use of As-based pesticides, industrial discharges (such as wood preservation that uses arsenic-based chemicals like chromated copper arsenate), and glass production, as well as improper disposal of waste containing As, like electronic waste or treated wood (Sang *et al.* 2021; Singh *et al.* 2021; Wang *et al.* 2022; Xie *et al*. 2022; Kumar *et al.* 2024). Combustion of coal is another major source of releasing As into the air, from which it can settle into water bodies through atmospheric deposition (Liu *et al*. 2019). Arsenic, a naturally occurring metalloid, is recognized as a potent carcinogen and poses severe risks to human health even at low concentrations (Bhowmick *et al*. 2014; Tanwei *et al*. 2018; Kim *et al.* 2019; Sang *et al.* 2021). According to the World Health Organization (WHO), long-term exposure to As can lead to various health issues, including skin lesions, internal cancers, and developmental effects (WHO 2022). Consequently, efficient methods for the removal of arsenate ions from contaminated water sources are urgently needed.

In recent years, there has been a growing interest in utilizing agricultural waste materials as cost-effective adsorbents for heavy metal removal from water. Studies show that agricultural wastes can effectively remove a wide range of heavy metals, including lead, cadmium, copper, and chromium, making them versatile for various water treatment needs (Kumar and Naidu 2019; Ademoyegun *et al.* 2022; Ogundiran *et al.* 2022). Many agricultural wastes contain natural components including cellulose, lignin, and hemicellulose, which have functional groups (such as hydroxyl, carboxyl, and amine groups) that can bind to heavy metal ions (Kumar and Naidu 2019; Liu *et al*. 2019; Ademoyegun *et al.* 2022; Ogundiran *et al*. 2022). These waste materials can be modified or activated to further enhance their metal-binding efficiency. Using agricultural waste for water purification promotes waste recycling and reduces the reliance on synthetic adsorbents that may not be biodegradable. This aligns with global efforts to promote green and sustainable technologies. Agricultural wastes, being readily available at low or no cost, offer a much cheaper alternative for water treatment. Agricultural waste materials, such as cassava waste, rice husks, sweet potato leaf, *Thaumatococcus danielli* leaves, sawdust, banana peels, eggshell waste, and coconut shells, are available in large quantities. They are renewable and can be used for heavy metal adsorption and thus provides a sustainable way to repurpose otherwise discarded materials (Kumar and Naidu 2019; Ofudje *et al.* 2020a, 2020b; Ademoyegun *et al*. 2022; Ogundiran *et al.* 2022).

Cassava is one of Nigeria's most significant crops, with the country consistently being the largest global producer. Nigeria produced approximately 60 million tonnes of cassava in recent years, making it the largest producer of cassava in the world **(**Ikuemonisan *et al*. 2020). This vast production of cassava has invariably led to the generation of a huge volume of cassava waste. The disposal of cassava waste is a challenge due to their bulk and potential environmental impact if left to decompose untreated. It is estimated that for every tonne of cassava processed, about 200 kg of solid waste is generated, alongside other by-products such as peels, chaff, liquid effluents, and wastewater. The large-scale production leads to substantial environmental challenges due to the improper disposal of this waste. Addressing this waste issue is crucial for improving environmental sustainability in the cassava production processes. Studies have demonstrated that cassava chaff contains several components, including silica and alumina, which possess favorable adsorption characteristics (Kumar and Naidu 2019; Sang *et al.* 2021). Unlike other adsorbents such as activated carbon or synthetic materials, cassava chaff ash does not require imported raw materials or complex supply chains to prepare. Cassava chaff ash can be produced through simple heat treatment, requiring minimal energy and infrastructure compared to high-energy processes for activated carbon or chemically modified adsorbents. It is more economical than other biomass-based adsorbents that rely on less accessible feedstocks like coconut shells or hardwood. Also, the use of cassava chaff promotes waste-to-resource principles, reducing agricultural waste while addressing environmental pollution. Unlike some other agricultural residues, cassava chaff is often underutilized, making this approach a novel and impactful way to repurpose waste.

The study addressed the critical knowledge gap in identifying and utilizing low-cost, sustainable, and locally available adsorbents for arsenic (As) removal from contaminated water. While numerous studies have focused on conventional adsorbents such as activated carbon, biochar, and synthetic materials, they often fail to meet the economic and resource constraints faced by developing regions. The study specifically investigates cassava chaff, a widely available and underutilized byproduct of cassava processing and examines cassava chaff as a precursor for adsorbent production, filling a gap in research on waste valorization for water treatment applications. While previous research has explored cassava residues such as peels and stems for adsorptive applications, the specific use of cassava chaff ash remains underexplored. Investigating cassava chaff ash as an adsorbent introduces a new avenue for valorizing agricultural waste, potentially leading to cost-effective and sustainable water treatment solutions. Also, since arsenic contamination in water poses significant health risks, its removal is a critical area of study. The application of cassava chaff ash for arsenic ion adsorption has not been extensively reported, making this study a pioneering effort in assessing its efficacy for this specific contaminant. The research thus promotes the concept of waste-to-resource by converting cassava chaff, an agricultural by-product, into a valuable adsorbent material, as this will not only address waste disposal issues but also contributes to the development of sustainable and eco-friendly water purification methods.

The aim of the study was to investigate the feasibility and effectiveness of using cassava chaff ash as a low-cost, sustainable adsorbent for the removal of arsenic ions from contaminated water. This involved a comprehensive analysis of the adsorption isotherms, adsorption kinetics, and thermodynamic properties. The study uniquely explored both raw cassava chaff and heat-treated cassava chaff ash, identifying how thermal processing influences adsorption efficiency, capacity, and mechanisms.

EXPERIMENTAL

Preparation of Arsenic Solution

The reagents used in this study were purchased from Merck, Germany and Loba Chemie Pvt. Ltd. India, and were of analytical grade. All solutions were prepared using double-distilled water, and pH adjustments were carried out with 0.1 M hydrochloric acid or sodium hydroxide solutions. A 1000 mg/L arsenic stock solution ($Na_2HAsO_4{\cdot}7H_2O$), which was sourced from Loba Chemie Pvt. Ltd. India was prepared. Working concentrations of arsenic standards were obtained through serial dilution of the stock solution.

Cassava Chaff Adsorbent Preparations

The preparation of ash adsorbent from cassava chaff is a process that transforms the waste by-product of cassava processing into a functional material capable of adsorbing As ions. This process involves several stages, including drying, burning (pyrolysis), sieving, and possible activation. Fresh cassava chaff, which is the fibrous by-product remaining after cassava processing (grating and pressing), were collected from a local cassava mill factory in Ifo town (Ogun State, Nigeria) and thoroughly washed using distilled water to remove odor and other dirt. The collected chaff was thereafter air-dried in the open laboratory for 14 days to remove moisture and then oven-dried at a temperature of 100 °C for 4 h to ensure complete combustion during the next stage of burning. The pyrolysis was done in a furnace at around 500 °C for 2 h. After burning, the remaining material, which was an ash, was sieved to obtain a finer, and more effective adsorbent and referred to as heat-activated cassava chaff ash (HACCA). The other portion that was not burnt was called cassava chaff raw (CCR).

Structural Elucidation

The structural elucidation of cassava chaff is crucial for understanding its composition, morphology, and potential functionality. In this study, characterization of cassava chaff ash was performed using Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX), X-ray Diffraction (XRD), and a Zetasizer Nano ZS instrument. The FT-IR analysis was used to identify the functional groups present in cassava chaff by detecting the vibrational modes of chemical bonds. For this study, the FT-IR spectra were recorded using a Bruker Tensor 27 spectrophotometer (USA). The sample was finely ground and mixed with potassium bromide (KBr) to form a pellet. The SEM-EDX analysis was performed using an EVO MA-10 (Carl Zeiss, Jena, Germany) electron microscope. This technique allowed for the visualization of surface morphology and the elemental composition of the ash. The crystalline structure of cassava chaff ash was analyzed using an X'PERT Pro PANalytical diffractometer with Cu Kα radiation (λ = 1.5406 Å). The XRD pattern provided insights into the mineral phases present in the ash. The Zetasizer Nano ZS (Malvern, UK) was employed to analyze the particle size distribution and zeta potential of the cassava chaff in suspension.

Adsorption Studies

About 25 mL of As solution was added into a conical flask containing 35 mg of powdered cassava chaff ash. The adjustment of the pH of the solution was made using 0.1 M HCl or NaOH, and the content was shaken using an orbital shaker at room temperature. After shaking, and at a pre-determined time interval, separation of the solid adsorbent from the filtrate was done by centrifugation at 3500 rpm for 10 min. The filtrate was analyzed for As content *via* atomic absorption spectroscopy (AAS) (iCE™ 3500, Thermo Fisher Scientific, Waltham, MA, USA). The experiment was done thrice, and the average values were recorded. The amount of As(V) adsorbed and the percentage adsorption were deduced from Eqs. 1 and 2 below,

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

$$R(\%) = \frac{C_o - C_e}{C_o} \times 100 \qquad (2)$$

where the As amount adsorbed is given as Qe (mg/g), As initial levels and equilibrium concentrations (mg/L) are represented as C_o and C_e, respectively, As volume utilized is denoted by V in L, whereas the mass of the cassava biomass used is denoted by m in g.

Desorption Study

After adsorption, cassava chaff adsorbents were separated from the As solution by immersing the used adsorbent in a desorbing agent using 0.1 M HCl. Thereafter, another subsequent adsorption cycle was performed and after a pre-determined time, the mixture was filtered and then the solution was analyzed for As concentration using AAS to evaluate adsorption-desorption efficiency. The adsorbent was regenerated by washing it with 0.1 M HCl and reuse in subsequent adsorption cycles to study its reusability. The desorption efficiency was calculated from Eq. 3:

$$Desorption\ Efficiency = \frac{Amount\ of\ As\ desorbed}{Amount\ A\ adsorbed}\ X\ 100 \qquad (3)$$

Statistical Methods

Multiple adsorption experiments under controlled conditions were conducted to gather a comprehensive dataset so as to ensure that variability due to experimental conditions was minimized. Thereafter, the average amount of adsorbate removed by the adsorbent across all experiments were computed and standard deviation was determined. Regression models were used to fit adsorption isotherms and kinetics to the experimental data. The goodness-of-fit was established via statistical metrics such as the coefficient of determination (R^2) and standard error.

RESULTS AND DISCUSSION

Structural Evaluations

The FT-IR spectra of raw cassava chaff before heat activation (Fig. 1a) showed a broad peak between 3200 and 3550 cm^{-1}. This range typically corresponds to O-H stretching vibrations, which are associated with hydroxyl groups (–OH). The broad nature of the peak suggests the presence of hydrogen bonding, which is likely from water or alcohol groups, such as those found in cellulose, hemicellulose, or lignin, which are abundant in cassava chaff. The peak seen at 1675 cm^{-1} can be assigned to C=O stretching vibrations, which suggests the presence of carbonyl groups, which could be from starch, lignin, or other polysaccharides that contain ester linkages or related groups. The peak found in the region of 1508 cm^{-1} is due to C=C stretching of aromatic ring vibrations and may suggest the presence of lignin or other aromatic compounds in the cassava chaff. The peak at 1025 cm^{-1} can be attributed to C-O stretching vibrations, which are typically seen in polysaccharides such as cellulose, hemicellulose, or starch. The observed peak at 989 cm^{-1} is due to the C-O stretching vibration, often associated with polysaccharides or glucosidic bonds found in cellulose and starch.

The FT-IR spectrum of heat-treated cassava chaff (Fig. 1b) reflects some changes in its chemical structure due to heat treatment. The weak peak at 3482 cm^{-1} falls in the region of O-H stretching, like the broad peak observed earlier, but its weakness suggests a reduction in hydroxyl groups or less extensive hydrogen bonding after heat treatment. This could indicate a loss of moisture (water content) or some degradation of polysaccharides (such as cellulose and hemicellulose) in which hydroxyl groups are present. Heat treatment can reduce the intensity of O-H stretching because of dehydration or structural modifications. The peak at 1664 cm^{-1} (weak peak) corresponds to C=O stretching vibrations (carbonyl groups), similar to the 1675 cm^{-1} peak in untreated cassava chaff. The shift to a lower wavenumber (from 1675 to 1664 cm^{-1}) and the weaker intensity suggests some thermal degradation of the carbonyl-containing compounds (such as ester linkages in starch or lignin). The reduction in intensity could also imply partial decomposition of these compounds. The peak seen at 1518 cm^{-1} is in the region of aromatic C=C stretching, which is characteristic of lignin. The peak is weaker compared to the untreated material (1508 cm^{-1}), suggesting some degradation or partial depolymerization of lignin due to the heat treatment. Lignin tends to undergo structural changes when exposed to high temperatures, leading to weakening of the aromatic ring vibrations. The observed peak at 1042 cm^{-1} (weak peak) is associated with C-O stretching in polysaccharides, namely cellulose and hemicellulose. The weak intensity suggests a degradation of carbohydrate structures, possibly from the breakdown of glycosidic bonds or the overall reduction in polysaccharide content due to heat. The shift from 1025 to 1042 cm^{-1} may indicate changes in the crystalline structure of cellulose or partial degradation of the material. The peak at 867 cm^{-1} correspond to C-H out-of-plane bending in polysaccharides or aromatic structures. The low intensity of this peak suggests a reduction in the amount of these structures, possibly due to thermal decomposition or pyrolysis effects caused by the heat treatment. Overall, the FT-IR spectrum shows that heat treatment causes some structural modifications in cassava chaff, with degradation or partial loss of hydroxyl groups, carbohydrates (cellulose/hemicellulose), and lignin.

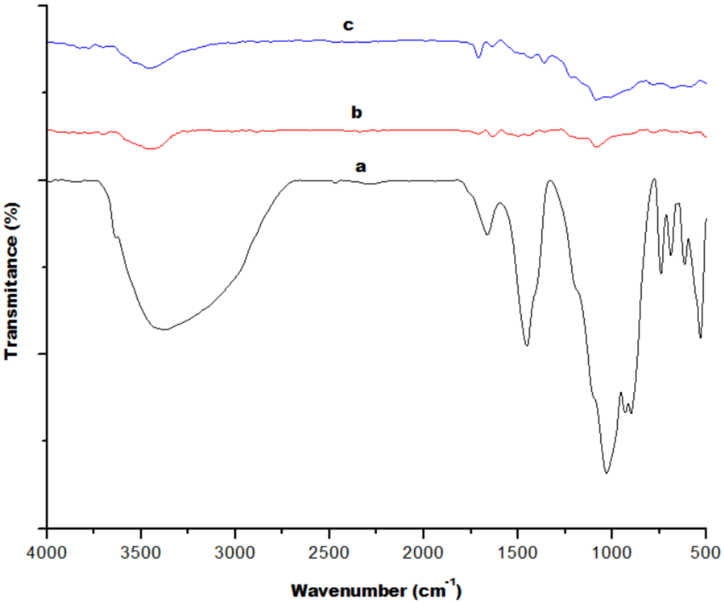


Fig. 1. FT-IR spectrum of (a) cassava chaff raw, (b) heat-activated cassava chaff ash (HACCA), and (c) heat-activated cassava chaff ash after adsorption

The FT-IR spectrum of heat-treated cassava chaff after the adsorption of a pollutant (Fig. 1c) suggests that there were interactions between the pollutant and the surface functional groups of the cassava chaff. For instance, the peak at 3475 cm^{-1} (moderate peak) corresponds to O-H stretching, similar to the 3482 cm^{-1} peak in the heat-treated sample. The peak had shifted slightly (from 3482 to 3475 cm^{-1}) and had a moderate intensity, indicating that there were still hydroxyl groups present, but they were likely involved in hydrogen bonding with the pollutant. The peak at 1652 cm^{-1} (also moderate peak) corresponds to C=O stretching vibrations, similar to the previous 1664 cm^{-1} peak in the heat-treated sample, but with a shift to a lower wavenumber (1652 cm^{-1}). The pollutant may have bonded to or adsorbed onto carbonyl-containing functional groups, suggesting that ester or carboxyl groups were involved in the adsorption process. The peak at 1505 cm^{-1} is associated with aromatic C=C stretching vibrations, likely from lignin in the cassava chaff. The peak at 1227 cm^{-1} could correspond to C-O stretching which may indicate the involvement of ester, or ether. The appearance of this peak, which was not present in the heat-treated sample before adsorption, suggests the formation of new bonds. Finally, the peak seen at 1047 cm^{-1} (moderate peak) is associated with C-O stretching, similar to the 1042 cm^{-1} peak in the heat-treated sample. The C-O groups may be interacting with the pollutant through hydrogen bonding or other weak interactions, suggesting that the carbohydrate matrix of the cassava chaff plays a role in pollutant adsorption.

The XRD data for cassava chaff before and after adsorptions can provide insights into the structural changes of the material. Before adsorption (Fig. 2a), peaks were seen at 2θ values of 15.02°, 21.3°, and 22.4°. These peaks are likely associated with the crystalline components of cassava chaff, which is primarily composed of cellulose, hemicellulose, lignin, and possibly starch. Typically, natural fibrous materials such as cassava chaff show characteristic peaks related to cellulose I. The peak at 15.02° (2*θ*) is commonly attributed to the ($\bar{1}\bar{1}0$) plane of cellulose I, a common crystalline form found in natural plant fibers. The peak at 21.3° (2*θ*) corresponds to the amorphous regions of cellulose or hemicellulose, indicating a less ordered structure. The peak observed at 22.4° (2*θ*) is often associated with the (200) plane of crystalline cellulose, indicating a higher degree of crystallinity. After adsorption (Fig. 2b), peaks were seen only at 15.06° and 22.1° of 2*θ*, indicating some changes to the XRD pattern. The slight shift from 15.02° to 15.06° suggests a minimal structural change or distortion in the cellulose I ($\bar{1}\bar{1}0$) plane due to the interaction with the pollutant. Further, the shift from 22.4° to 22.1° could indicate a reduction in the crystallinity of the material, possibly due to the adsorption process. The pollutant might have interacted with the cellulose structure, causing partial disruption or rearrangement of the crystalline regions as previously noted for FT-IR analysis. Peaks corresponding to functional groups such as -OH, carbonyl C=O, and C=C suggest active adsorption sites which could lead to the binding of arsenic As(V) through hydrogen bonding, ion exchange, or complexation adsorption mechanism. After adsorption process, the FT-IR analysis shows shifts in these peaks, indicating interaction with arsenic ions, confirming specific adsorption mechanisms like chemisorption or physisorption.

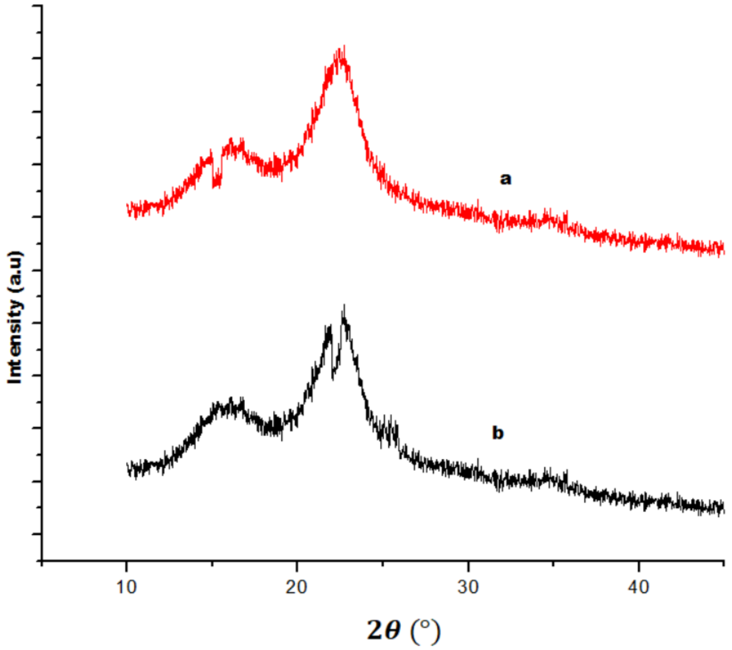
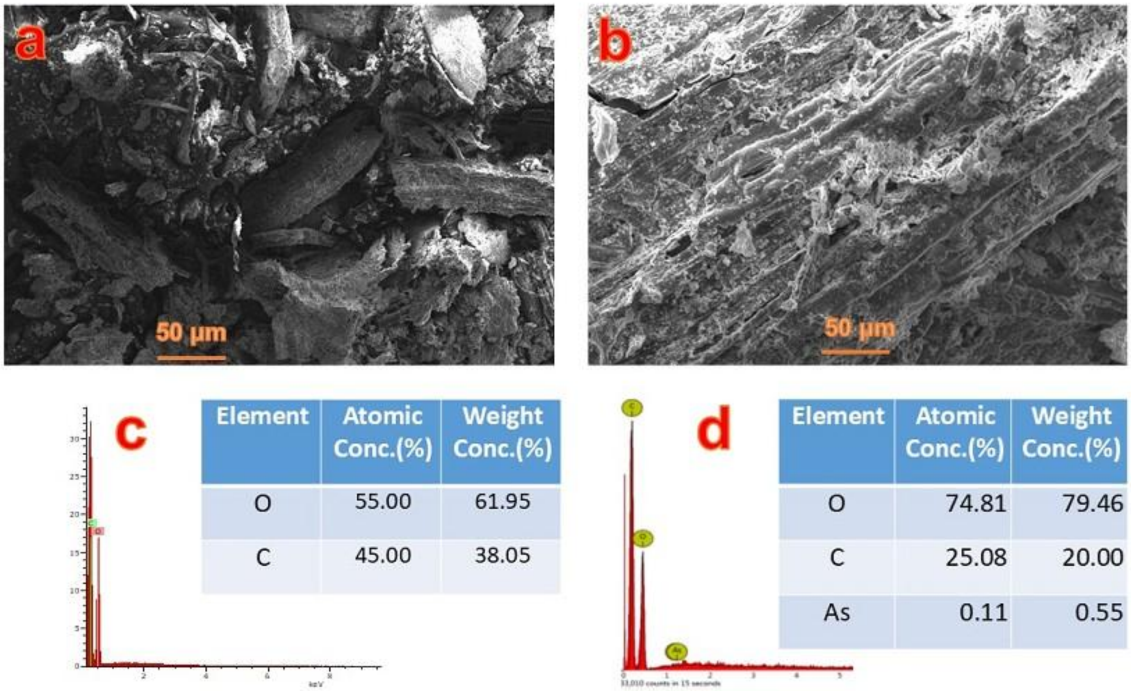


Fig. 2. XRD of (a) cassava chaff prior to adsorption, and (b) cassava chaff after adsorption

The peaks' shifts and slight changes in intensity suggest that the adsorption of the pollutant onto the cassava chaff caused some structural modification, particularly in the crystalline regions. The reduction in crystallinity (shift from 22.4° to 22.1°) may indicate that the pollutant is interacting with the more ordered regions of the material, leading to disruption or swelling of the crystalline cellulose. However, the persistence of the peak around 15.02° (shifting to 15.06°) suggests that the adsorption did not completely alter the basic cellulose structure, but there were small perturbations, possibly due to surface interactions. In summary, the XRD data showed that the cassava chaff retained some of its crystalline cellulose structure after adsorption, but the shifts in peak positions reflect changes in crystallinity and internal structure, likely due to the interaction with the pollutant. The adsorption XRD analysis after the uptake of As(V) reveals changes in peak intensity as well as the appearance of new peaks, suggesting the formation of arsenic-containing surface complexes or precipitation.

Scanning electron microscopy was used to examine the surface morphology of the cassava chaff before and after adsorption, and some changes in the surface texture, porosity, and structure due to the adsorption process were seen, as indicated in Fig. 3. Before the adsorption process (Fig. 3a), the surface texture of the cassava chaff had a rough, porous surface with a fibrous structure, which is typical of natural agricultural waste materials. The natural porosity of the cassava chaff was evident, with visible pores and cavities that are necessary for the adsorption process. These pores act as active sites where adsorption can occur. However, after the adsorption process, the surface was observed to have been covered with adsorbed particles or contaminants. Additionally, the pores and cavities were less visible due to the blockage or filling with the adsorbate molecules, leading to a smoother or denser appearance. The SEM images after adsorption showed a marked difference, with evidence of the adsorbed materials on the surface, and potentially a reduction in visible porosity due to filling of the natural cavities in the cassava chaff and these changes help confirm successful adsorption.



Element	Atomic Conc.(%)	Weight Conc.(%)
O	55.00	61.95
C	45.00	38.05

Element	Atomic Conc.(%)	Weight Conc.(%)
O	74.81	79.46
C	25.08	20.00
As	0.11	0.55

Fig. 3. Surface morphology of (a) cassava chaff prior to adsorption, (b) cassava chaff after adsorption, (c) EDX of cassava chaff prior to adsorption, and (d) EDX of cassava chaff after adsorption

Results of the EDS technique for determination of the elemental composition of the cassava chaff before and after the uptake of As are shown in Fig. 3c and d respectively. The EDX results suggest that the cassava chaff consisted primarily of carbon and oxygen. The higher atomic concentration of carbon (61.95%) compared to oxygen (38.05%) reflects the fact that carbon is a smaller and lighter element than oxygen, meaning more carbon atoms are present even though their total mass is similar to that of oxygen. This composition is typical of organic materials such as cassava chaff, which mainly consist of carbon-based compounds (such as cellulose and lignin) and oxygen atoms bound in functional groups (*e.g.*, hydroxyl groups, oxygen-containing compounds). After the uptake process, the presence of As was detected as shown in Fig. 3d confirming the incorporation of As molecules onto the surface of the adsorbent.

The Role of Contact Time and Initial Metal Concentrations

The influence of contact time on the adsorption capacity of As using cassava chaff in its raw form as an adsorbent is shown in Fig. 4. At 50 mg/L of adsorbate concentration, on increasing the contact time from 10 min to 150 min, the adsorption capacity increased from 5.66 mg/g to 21.3 mg/g, suggesting that more As ions were able to interact with the available active sites on the cassava chaff, leading to greater adsorption (Ofudje *et al.* 2020a). Beyond 150 min, there was no further increase in adsorption capacity, indicating that equilibrium had been reached. At this point, all the available adsorption sites on the cassava chaff were likely occupied, and no additional arsenic ions could be adsorbed (Ofudje *et al.* 2020a). At a higher initial concentration of arsenic (300 mg/L), the adsorption capacity increased from 26.3 mg/g to 79.6 mg/g as the contact time increased from 10 to 150 min. This indicates that higher As concentrations provide a greater driving force for mass transfer, allowing more As ions to occupy the adsorption sites (Ademoyegun *et al*. 2022). Hence, the cassava chaff can adsorb more As when its initial concentration is higher. The sharp rise in capacity under higher concentrations reflects that cassava chaff has a relatively high capacity for As(V) when challenged with sufficient adsorbate.

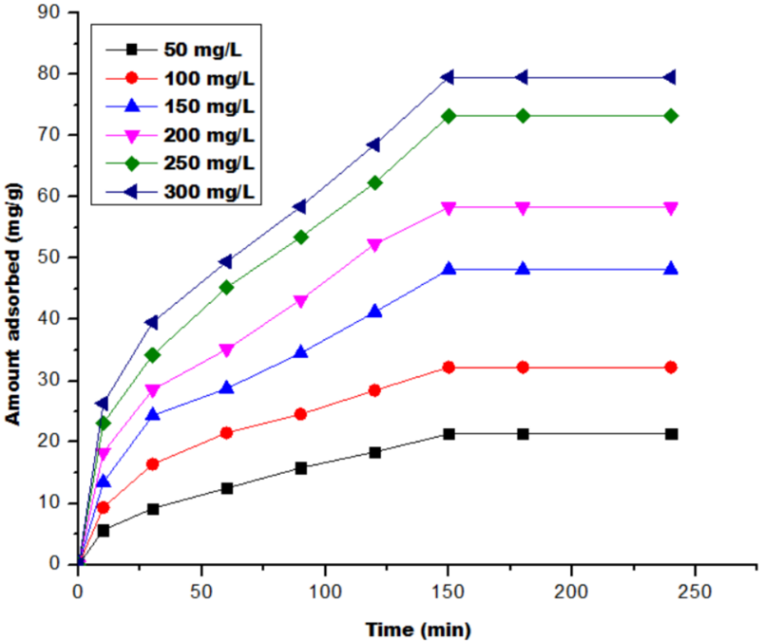


Fig. 4. Plots of As(V) amount adsorbed against contact time by cassava chaff raw

The results regarding the effects of contact time on As(V) adsorption using heat-treated cassava chaff present interesting insights into how thermal treatment enhances adsorption performance, as depicted in Fig. 5. The adsorption capacity increased from

9.28 to 24.50 mg/g when the contact time was extended from 10 min to 120 min and at 50 mg/L of As(V) concentration. This increase indicates that more arsenic ions were adsorbed as time progressed, similar to the behavior observed with raw cassava chaff. However, it is important to note that the initial adsorption capacity (9.28 mg/g) was higher than that of the raw cassava chaff (5.66 mg/g), suggesting that heat treatment improved the adsorbent’s performance by increasing the availability of active adsorption sites or enhancing the surface properties. After 120 min, no further increase in adsorption capacity was observed, indicating that equilibrium had been achieved. The shorter time to reach equilibrium (120 min as against 150 min for raw chaff) suggests that heat treatment may have accelerated the adsorption kinetics by making the adsorption process more efficient. This could be due to modifications in the chaff’s pore structure or surface chemistry, resulting in faster and more effective binding of As(V) ions to the available sites. Equilibrium was reached at 120 min for the heat-treated chaff, whereas it took 150 min for the raw chaff. This indicates that heat treatment not only improved the adsorption capacity but also enhanced the rate of arsenic uptake, making the process more efficient.

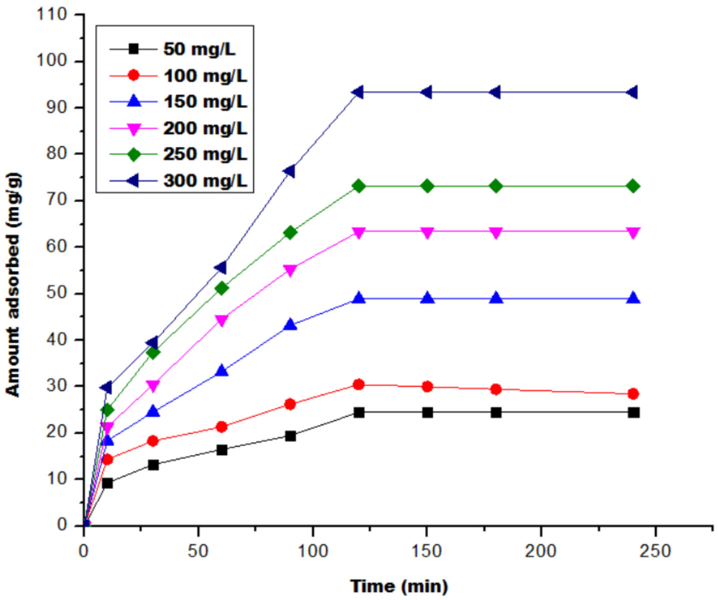


Fig. 5. Plots of As(V) amount adsorbed against contact time by heat activated cassava chaff

At a higher initial arsenic concentration of 300 mg/L, the adsorption capacity increased from 29.8 to 93.4 mg/g as the contact time increased from 10 to 120 min. This rise in adsorption capacity highlights the improved performance of heat-treated cassava chaff, especially under higher arsenic concentrations. The increase from 29.8 mg/g (at 10 min) to 93.4 mg/g (at 120 min) suggests that the heat treatment enhanced the chaff’s capacity to handle higher concentrations of arsenic, potentially by increasing the porosity or activating functional groups that interact with arsenic ions. This demonstrates the superior ability of heat-treated cassava chaff to remove As from solutions, especially in cases where high levels of contamination are present.

Heat-treated cassava chaff (cassava chaff ash) outperformed raw cassava chaff in arsenic adsorption due to a combination of factors, including increased surface area, enhanced porosity, and changes in chemical activity. During heat treatment, volatile organic compounds and moisture in the raw cassava chaff are removed, leaving behind a more porous structure. This enhances the surface area available for arsenic ions to interact with the adsorbent. The increased porosity creates more adsorption sites and improves mass transfer efficiency. Similarly, heat treatment often leads to the development of micropores and mesopores in the material, which are critical for adsorbing small molecules such as arsenic ions. Heat treatment could as well decompose the organic components (*e.g.*, cellulose, hemicellulose), as evidenced through the FTIR analysis in cassava chaff, exposing and activating functional groups that play a key role in arsenic binding. Ash from heat-treated cassava chaff often contains oxides (*e.g.*, silica, alumina) and activated functional groups like hydroxyl (-OH) and carbonyl (C=O), which can form strong complexes with arsenic ions, thus enhancing the adsorption performance. Also, heat-treated materials are more chemically stable, allowing them to sustain adsorption performance even under varying pH conditions.

The Effect of pH

The results on the effect of pH on As adsorption using raw and heat-treated cassava chaff reveal the critical role pH plays in influencing the adsorption efficiency. The data show some variation in arsenic adsorption efficiency across different pH levels, as depicted in Fig. 6.

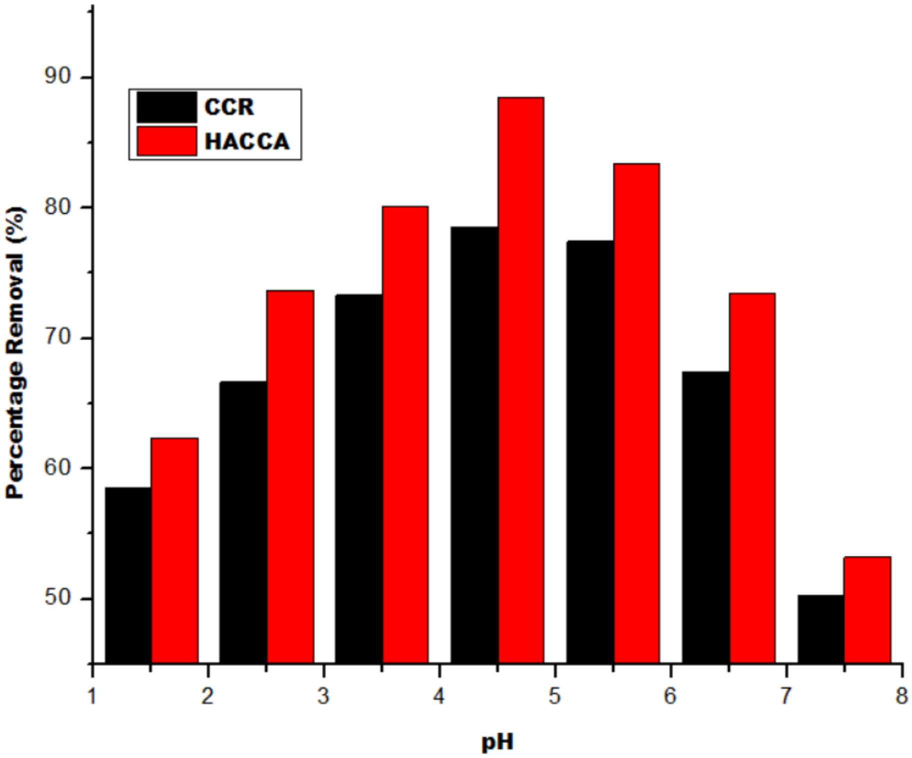


Fig. 6. Plots of percentage removal of As(V) against pH by CCR and HACCA

The percentage adsorption of arsenic by the raw sample rose from 58.5% to 78.6% as the pH was increased from 1.5 to 4.5, while that of the heat-treated chaff increased from 62.3% to 88.4%. This indicates that the acidic environment at lower pH values (around 1.5 to 4.5) favored As adsorption. The improvement in adsorption efficiency with rising pH up to 4.5 suggests that this pH range was optimal for the interaction between the cassava chaff surface and arsenic species. The possible mechanism for this behavior is that at lower pH (1.5), the surface of the adsorbent (cassava chaff) is likely highly protonated (positively charged due to the presence of H^+ ions in solution) (Ofudje *et al*. 2021). This can enhance the attraction between the positively charged surface and the negatively charged arsenic species, particularly arsenate (AsO_4^{3-}) or arsenite (AsO_2^-) ions. However, as the pH rises towards 4.5, this protonation effect is still present, but at a more balanced level, creating optimal conditions for arsenic adsorption by maximizing the electrostatic attraction between the adsorbent and the adsorbate (Attinti *et al*. 2013; Liu *et al*. 2019).

Furthermore, as the pH increased from 4.5 to 7.5, the percentage adsorption decreased to 50.3% and 53.2% for raw and heat-treated samples, respectively. This decline suggests that at higher pH levels, the adsorbent surface became less protonated, reducing the electrostatic attraction between the adsorbent and arsenic ions (Attinti *et al*. 2013; Liu *et al*. 2019). In fact, at alkaline or near-neutral pH values (above 7), the surface of the cassava chaff could become negatively charged, leading to repulsion between the negatively charged adsorbent surface and arsenic anions (AsO_4^{3-}) (Liu *et al*. 2019). The possible mechanism for this behavior is that as the pH increases, hydroxyl ions (OH^-) in the solution increase, potentially competing with arsenic species for the adsorption sites on the cassava chaff surface. Additionally, at higher pH, the dissociation of arsenic species may change, influencing their interaction with the adsorbent. For example, arsenic may exist in different forms (arsenate or arsenite ions), and the affinity of these forms for the cassava chaff surface may vary depending on the pH (Liu *et al*. 2019). Attinti *et al*. (2013) observed the maximum adsorbed amount and removal efficiency of As(V) to be 1.96 mg/g and 98.2% at pH 3.0, and this was attributed to surface charges of adsorbent and various arsenic species at different pH values. It was observed that the heat-treated cassava chaff performed better in acidic environments, but the higher initial percentage adsorption (62.3%) at pH 1.5 and greater maximum adsorption (88.4%) at pH 4.5 suggest that heat treatment had enhanced the adsorbent's overall performance.

Furthermore, at higher pH, the negatively charged arsenic ions ($HAsO_4^{2-}$, AsO_4^{3-}) were repelled by the negatively charged surface of the adsorbent and as such, the arsenic ions which initially bound to the surface *via* electrostatic attraction or weak hydrogen bonding may detach, leading to desorption. Desorption under alkaline conditions can release previously adsorbed arsenic back into the solution, reducing the long-term effectiveness of the adsorbent. Desorption risks increase as pH moves above ~8, where most functional groups on the adsorbent surface lose their ability to interact effectively with arsenic ions. The implications for field in real-world scenarios is that in natural water sources often have varying pH levels due to geological and environmental factors (*e.g.*, acidic mining runoff or alkaline groundwater). For effective adsorption, maintaining the solution pH within the optimal range (~4.5 to 7) is crucial. Alkaline water sources may require pre-treatment (*e.g.*, acidification) to lower the pH and improve adsorption efficiency. In field applications, systems operating in high-pH environments risk arsenic leaching from spent adsorbents back into the treated water and this desorption could compromise the safety of the treated water and require additional safeguards, such as monitoring pH during treatment or stabilizing the spent adsorbent to prevent arsenic release.

The Effect of Adsorbent Dosage

The results on the effect of adsorbent dosage on arsenic (As) adsorption using cassava chaff demonstrated a complex relationship between adsorbent dosage and adsorption efficiency, as can be seen in Fig. 7. It was observed that the percentage adsorption of arsenic increased from 52.3% to 77.5% as the dosage of raw cassava chaff was increased from 10 to 45 mg, whereas in case of heat-treated sample, the percentage adsorption of As increased from 56.7% to 84.6% as the adsorbent dosage was increased from 10 to 35 mg. This increase suggests that adding more adsorbent initially provides a greater surface area and more active sites for As to bind, resulting in higher adsorption efficiency (Ofudje *et al*. 2020b; Ademoyegun *et al*. 2022). At lower dosages (10 mg), the available adsorption sites on the cassava chaff are limited, leading to less effective arsenic removal and a lower percentage of adsorption (Ofudje *et al*. 2020b; Ademoyegun *et al*. 2022). However, as the dosage increases, more adsorption sites become available, allowing more As ions to be adsorbed. This leads to a higher percentage of arsenic removal, as the adsorbent can handle a larger portion of the contaminant.

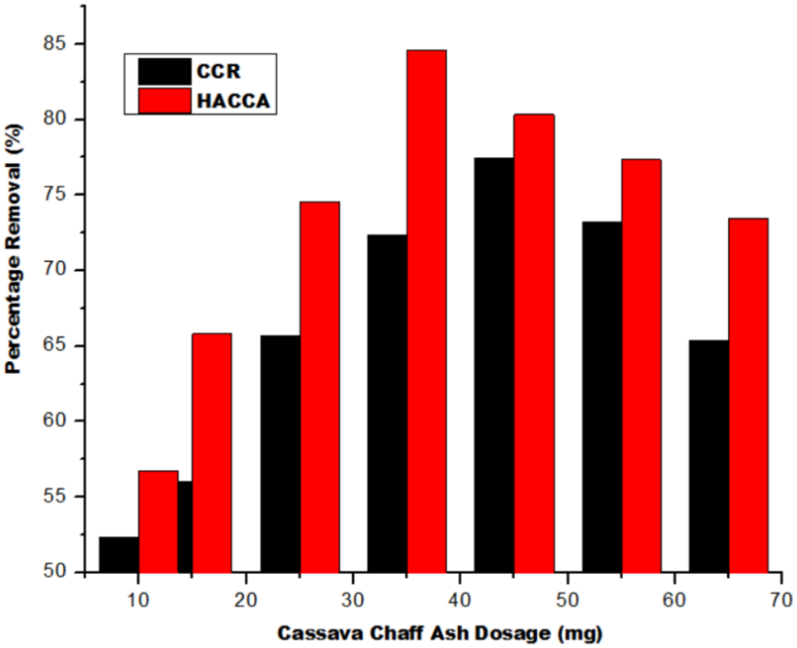


Fig. 7. Plots of percentage removal of As(V) against biomass dosage

The heat treatment of the cassava chaff greatly improved the adsorption efficiency. The higher initial adsorption (56.7%) and the higher peak (84.6%) compared to raw cassava chaff (52.3% and 77.5%) suggest that heat treatment enhanced the adsorptive properties of the cassava chaff. Beyond a dosage of 35 or 45 mg, the percentage adsorption decreased when the adsorbent dosage was further increased. As the adsorbent dosage increased, the available arsenic in the solution may not be sufficient to occupy all the additional adsorption sites and this can result in a lower percentage adsorption because the total amount of As remains constant, and the ratio of adsorbate to adsorbent decreases (Ogundiran *et al*. 2022). In addition, at higher dosages, adsorbent particles may start to aggregate, reducing the effective surface area available for adsorption and this can lead to a decrease in adsorption efficiency as the active sites become less accessible to the arsenic ions (Liu *et al*. 2019; Ademoyegun *et al*. 2020).

Kinetic Modelling

Kinetic models are essential for understanding the adsorption mechanisms and predicting the adsorption rate of contaminants like As onto adsorbents such as raw cassava chaff and heat-treated sample. The pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic models were applied to describe the adsorption process.

Pseudo-first-order kinetic model (PFOKM)

The PFOKM assumes that the rate of adsorption is directly proportional to the number of available adsorption sites. The equation is given as (Adeogun *et al.* 2012),

$$\mathrm{In}\,(Q_e - Q_t) = InQ_e - kt \tag{4}$$

where Q_t is the amount of As adsorbed at time *t* (mg/g), Q_e is the amount of As adsorbed at equilibrium (mg/g), and k_1 is the rate constant of PFOKM (min^{-1}). The constants were deduced from Fig. 8a, and the values are listed in Table 1.

Pseudo-second-order kinetic model (PSOKM)

The pseudo-second-order kinetic model assumes that the adsorption rate is proportional to the square of the number of available adsorption sites and the equation is given as (Adeogun *et al.* 2012; Attinti *et al.* 2013),

$$t/_{Q_t} = 1/_{k_2}\, Q_e^2 + t/_{Q_e} \tag{5}$$

where k_2 is the rate constant of PSOKM (g/mg·min) and other parameters are as previously defined. The constants were deduced from Fig. 8b and the values listed in Table 1. In As adsorption on raw cassava chaff, the calculated adsorption capacity (Q_e) from the PSOKM provided a better match with the experimental data. The coefficient of determination (R^2) for the PFOKM ranged from 0.954 to 0.997, indicating a fairly good fit. However, the PSOKM had even higher values, ranging from 0.987 to 0.998, suggesting that it provided a much better representation of the adsorption kinetics. The sum of squared errors (%SSE) for the PFOKM ranged from 0.106 to 0.126, while for the PSOKM, it was much lower, ranging from 0.003 to 0.019. Lower %SSE values indicate that the second-order model was more accurate in predicting the experimental data, further supporting the conclusion that the second-order model was more appropriate for describing arsenic adsorption onto raw cassava chaff. The PFOKM rate constant (k_1) ranged from 0.016 to 0.2167 min^{-1}, while the PSOKM ranged from 0.105 to 0.931 g/mg·min. The higher values of k_2 suggest that the adsorption process follows second-order kinetics more closely, with a faster overall rate of adsorption compared to first-order kinetics.

In the case of the heat-treated sample, the PFOKM had R^2 values ranging from 0.987 to 0.998, indicated a nearly perfect fit to the experimental data in comparison with the PSOKM that had R^2 values ranging from 0.995 to 0.997, suggesting that both models can be employed to describe the adsorption behaviour of the pollutant.

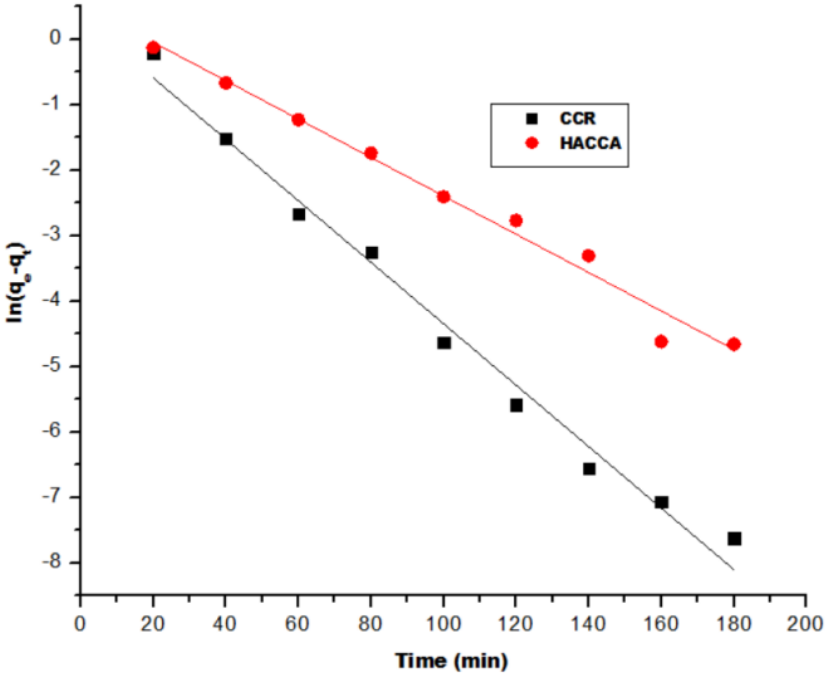


Fig. 8a. Plots of PFOKM for the adsorption of As(V) by CCR and HACCA

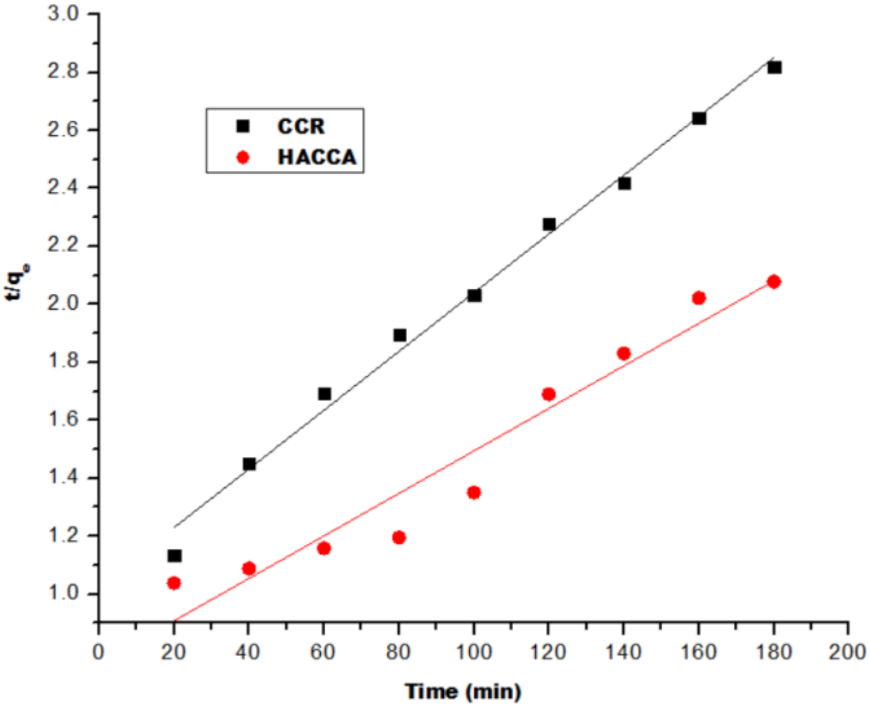


Fig. 8b. Plots of PFOKM for the adsorption of As(V) by CCR and HACCA

The PFOKM exhibited very low SSE values (0.002 to 0.011), indicating that it accurately predicted the adsorption behavior with minimal error. In contrast, the PSOKM had higher SSE values (0.052 to 0.092), suggesting that it deviated more from the experimental data. The lower SSE values for the first-order model indicate that it is the more appropriate model for describing this adsorption process.

Table 1. Physical Variables of PFOKM and PSOKM for the Adsorption of As (V) by CCR and HACCA

HACCA										
	First-Order						**Second-Order**			
C_o (mg/L)	C_e (mg/L)	$Q_{e(exp)}$ (mg/g)	$Q_{e(cal)}$ (mg/g)	k_1 (min^{-1})	R^2	SSE (%)	$Q_{e(cal)}$ (mg/g)	k_2 (gmg^{-1} min^{-1})	R^2	SSE (%)
50	33.24	24.5	25.02	0.023	0.998	0.009	19.46	0.015	0.951	0.092
100	56.33	30.46	31.22	0.038	0.998	0.011	26.23	0.017	0.992	0.062
150	84.33	48.93	49.12	0.042	0.989	0.002	43.22	0.024	0.987	0.052
200	103.22	63.41	63.03	0.063	0.996	0.003	55.33	0.042	0.997	0.057
250	144.32	73.24	74.55	0.071	0.987	0.008	63.23	0.048	0.979	0.061
300	183.44	93.41	95.62	0.093	0.996	0.011	76.44	0.065	0.994	0.081
CCR										
	First-Order						**Second-Order**			
C_o (mg/L)	C_e (mg/L)	$Q_{e(exp)}$ (mg/g)	$Q_{e(cal)}$ (mg/g)	k_1 (min^{-1})	R^2	SSE (%)	$Q_{e(cal)}$ (mg/g)	k_2 (g mg^{-1} min^{-1})	R^2	SSE (%)
50	23.44	21.33	15.8	0.015	0.954	0.116	20.44	0.105	0.997	0.019
100	43.22	32.22	24.55	0.0245	0.955	0.106	30.99	0.216	0.998	0.017
150	65.22	48.15	34.55	0.0375	0.973	0.126	49.021	0.486	0.988	0.008
200	75.32	58.33	43.22	0.0396	0.997	0.116	57.01	0.591	0.987	0.010
250	98.333	73.22	53.44	0.1547	0.967	0.121	72.55	0.726	0.989	0.004
300	123.13	79.55	58.44	0.2167	0.955	0.119	80.04	0.931	0.998	0.003

Adsorption Isotherms

When analyzing the adsorption of As onto cassava chaff, two common adsorption isotherm models were applied, which are the Langmuir and the Freundlich isotherms. These isotherms can help in understanding how adsorption occurs on the surface of an adsorbent, and their fit to experimental data helps in understanding the adsorption mechanism.

Langmuir Isotherm Model (LIM)

The Langmuir isotherm assumes that adsorption occurs on a homogenous surface with a finite number of identical sites, and that once a site is occupied, no further adsorption can occur on that site, proposing that adsorbed molecules do not interact with one another, as shown in Eq. 6 (Adeogun *et al*. 2012; Ofudje *et al*. 2019):

$$\frac{C_e}{Q_e} = \frac{1}{K_L q_L} + \frac{C_e}{q_L} \tag{6}$$

The Langmuir separation factor, which is represented as R_L, is given as (Adeogun *et al*. 2012),

$$R_L = \frac{1}{1+K_L C_o} \tag{7}$$

where Q_e is the amount of As (V) per unit mass of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L) of the As (V), Q_{max} is the maximum adsorption capacity (monolayer capacity) (mg/g), and K_L is the Langmuir constant related to the affinity of binding sites. The constants were deduced from Fig. 9a, and the values are listed in Table 2. The maximum amounts of As (Q_{max}) that could be adsorbed per unit mass of cassava chaff raw and heat-treated cassava chaff were 82.2 mg/g and 101 mg/g, indicating that heat treatment improved adsorption capacity of the biomass. The values of the separation factor, R_L, of the LIM obtained were 0.163 and 0.520 for raw and heat-treated samples, respectively, indicating that the adsorption was favorable because $R_L < 1$ (Adeogun *et al.* 2012; Attinti *et al.* 2013). The coefficient of determination, R^2, which shows how well the experimental data fits the Langmuir model, was close to 1, thus indicating a good fit (R^2 = 0.967 and 0.988 for raw and heat-treated cassava chaff, respectively). The high value of R^2 indicates that the Langmuir model fit the experimental data very well for the heat-treated cassava chaff when compared with raw sample, implying a monolayer adsorption process.

Freundlich Isotherm Model (FIM)

In contrast, the Freundlich isotherm is an empirical model that assumes adsorption occurs on a heterogeneous surface with non-uniform distribution of adsorption heat over the surface. It also allows for multilayer adsorption, and the strength of adsorption decreases as more sites are occupied.

Freundlich isotherm equation is given as (Ademoyegun *et al*. 2022; Ogundiran *et al*. 2022),

$$lnQ_e = lnK_F + {}^{1}\!/_{n}\, lnC_e \tag{8}$$

where K_F is the Freundlich constant indicative of the adsorption capacity, $1/n$ is a constant indicative of the adsorption intensity, and C_e is the equilibrium concentration of the adsorbate in solution. The constants were deduced from Fig. 9b, and the values are listed in Table 2. The adsorption intensities ($1/n$) found were 0.637 and 0.332 for cassava chaff raw and heat-treated cassava chaff, respectively, and because the values were between 0 and 1, it indicates favorable adsorption. The lower value of adsorption intensity of the heat-treated sample compared to the raw chaff suggests stronger adsorption interactions for the heat-treated chaff, implying higher surface heterogeneity and stronger binding sites. A lower value of $1/n$ indicates more heterogeneity in the adsorption process (Adeogun *et al.* 2012; Attinti *et al*. 2013).

Through fitting the experimental data using the coefficient of determination, R^2, for the Freundlich model (R^2 = 0.989 and R^2 =0.965 for raw and heat-treated sample, respectively), indicating the Freundlich isotherm provided a better fit to the experimental data for arsenic adsorption onto raw cassava chaff, indicating a heterogeneous adsorption surface and possibly multilayer adsorption. Because the Freundlich model accounts for adsorption on heterogeneous surfaces, this suggests that the surface of the raw cassava chaff may be non-uniform, with varying adsorption energies. Conclusively, the Langmuir isotherm suggests that As adsorption occurs as a monolayer on a homogenous surface for the samples treated with heat.

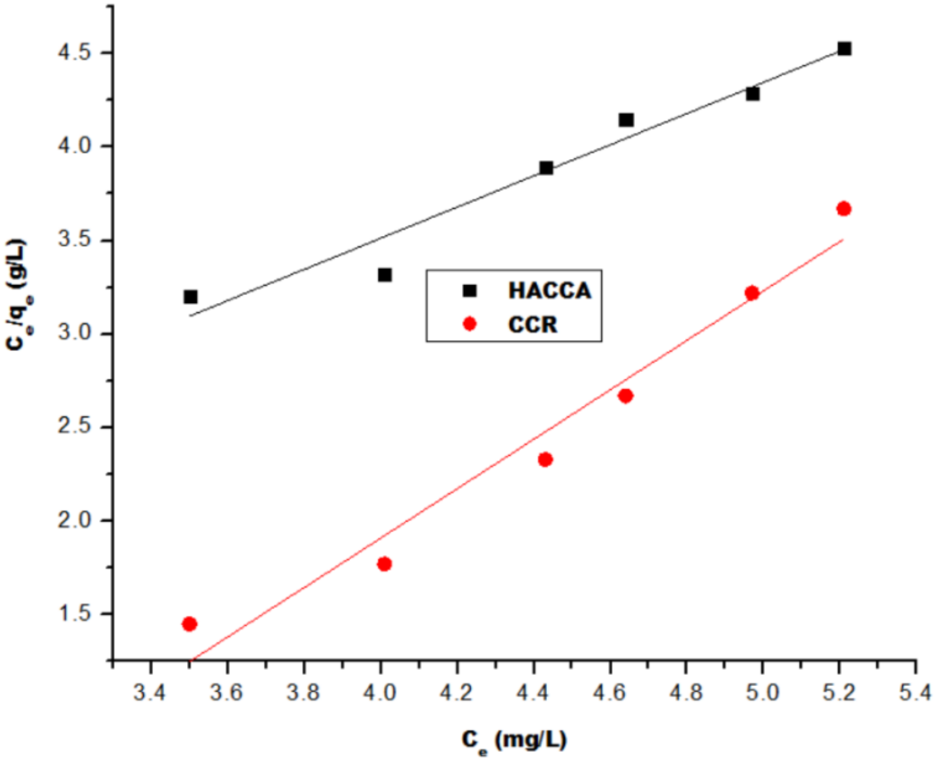


Fig. 9a. Plots of Langmuir isotherm for the adsorption of As (V) by CCR and HACCA

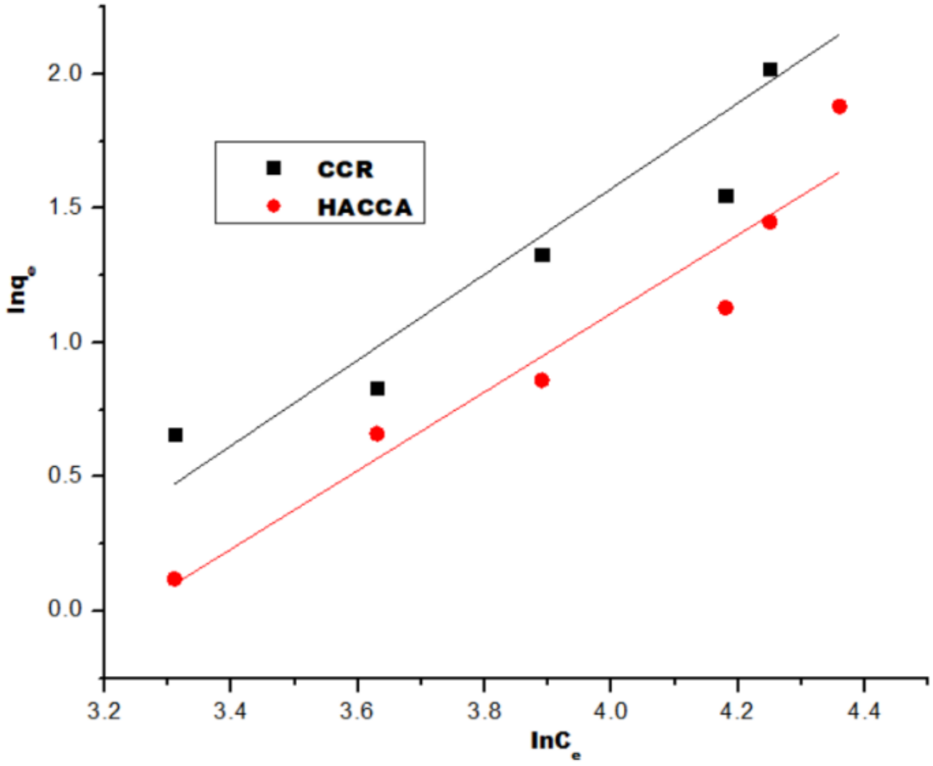


Fig. 9b. Plots of Freundlich isotherm for the adsorption of As (V) by CCR and HACCA

On the other hand, the Freundlich isotherm suggests a more complex adsorption mechanism involving a heterogeneous surface and possibly multilayer adsorption and may be more realistic for natural materials like cassava chaff, which likely have a diverse range of active sites. The comparison of the maximum adsorption capacity of cassava chaff with other literature adsorbents as indicated in Table 3 shows that cassava chaff adsorbent is a potential material for elimination of As (V) from contaminated wastewater.

Table 2. Variable Values from the Isotherm Models of Adsorption of As(VI) by Cassava Chaff

	Parameters	CCR	HACCA
Langmuir	Q_{max} (mg/g)	82.150	101.22
	R_L	0.163	0.520
	b (mg/L)	0.241	0.335
CCR	R^2	0.967	0.988
Freundlich	K_F (mg/g)(mg/L)$^{-1/2}$	55.330	76.388
	$1/n$	0.637	0.332
	R^2	0.989	0.965

Table 3. Comparison of the Maximum Adsorption Capacity of Cassava Chaff with Other Literature Adsorbents

Adsorbents	Adsorption Capacity (mg/g)	References
Goethite/silica nanocomposite	17.64	Attinti *et al*. 2013
Anatase nanoadsorbent	16.98	Kocanas-Atakl and Yurum 2013
Oxide shell free nZVI	153.6	Tucek *et al*. 2017
Micro/nanostructured MnO_2 spheres	14.50	Zhang and Sun 2013
Raw sludge	40.98	Huiping *et al.* 2020
Granular adsorbent	14.955	Huiping *et al*. 2020
Macroporous anion exchanger-supported Fe-Mn binary oxide	13.2	Li *et al*. 2012
Calcium alginate beads (G)	42.4	Hassan *et al*. 2014
G/activated carbon composite beads	66.7	Hassan *et al*. 2014
Sulfur modified nZVI	79.37	Singh *et al.* 2021
Iron oxide/activated carbon	20.24	Yao *et al*. 2014
Activated carbon	17.86	Yao *et al*. 2014
CCR	82.150	This study
HACCA	101.22	This study

Effects of Temperature and Evaluations of Thermodynamics Variables

The results on the effects of temperature on As adsorption using cassava chaff highlight the temperature-dependent nature of the adsorption process. The findings revealed how temperature influences the adsorption efficiency, which can help understand the thermodynamics of As adsorption, as shown in Fig. 10. The percentage adsorption when raw chaff was used increased from 50.4% to 75.5% when the temperature was increased from 298 K (25 °C) to 318 K (45 °C), whereas for the heat-treated sample, it increased from 56.7% to 82.3% when the temperature was increased from 298 K (25 °C) to 313 K (40 °C). This increase in adsorption efficiency with rising temperature indicates that the adsorption process was endothermic within this temperature range (Ofudje *et al.* 2021; Ademoyegun *et al*. 2022). In an endothermic process, adsorption is enhanced as temperature increases, suggesting that higher temperatures facilitate better interaction between arsenic ions and the adsorbent (cassava chaff).

Cassava chaff ash, being heat-treated, is thermally stable under moderate temperature variations. However, exposure to extreme temperatures (*e.g.*, very high heat or freezing conditions) could impact its structural integrity over time, as prolonged exposure to excessive heat (beyond what is typical for tropical climates) might cause sintering or further thermal degradation of the ash, reducing its porosity and adsorption capacity. However, at lower temperatures, freezing conditions might lead to microcracks or changes in the structural matrix if the adsorbent retains residual moisture, potentially affecting its longevity. Thus, in regions with fluctuating temperatures (*e.g.*, deserts with hot days and cold nights), adsorption systems may need insulation or temperature stabilization to ensure consistent performance. Seasonal variations might require adjustments in operational parameters, such as dosing rates or exposure times. Also, coating cassava chaff ash with thermally stable materials (*e.g.*, silica or polymers) could enhance its durability and maintain performance across temperature ranges.

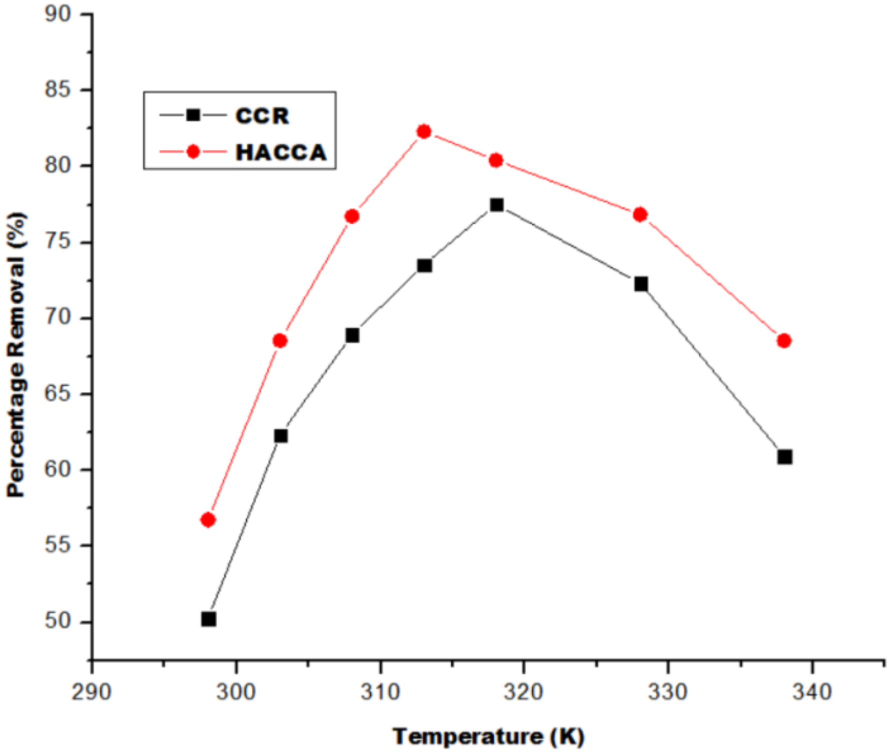


Fig. 10. Plots of percentage removal of As (V) against temperature

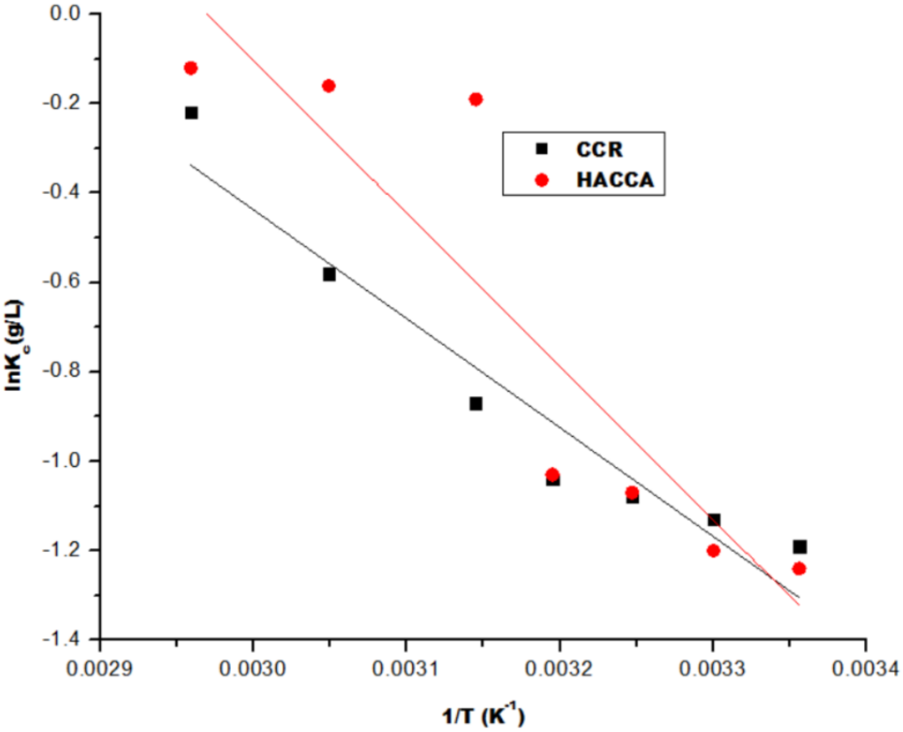


Fig. 11. Plots of thermodynamic parameters

However, when the temperature was further increased to 338 K (65 °C), the percentage adsorption decreased, and this drop in adsorption efficiency at higher temperatures indicates that, beyond a certain temperature, the adsorption process becomes less efficient, suggesting that excessively high temperatures negatively affect the adsorption process. At higher temperatures (338 K), the binding forces between the As ions and the adsorbent surface may weaken, leading to desorption and this means that some of the arsenic ions previously adsorbed may be released back into the solution due to the thermal energy overcoming the adsorptive forces. High temperatures could cause structural changes or thermal degradation of the cassava chaff adsorbent, reducing its capacity to adsorb arsenic ions and this could lead to fewer available active sites for As adsorption. Thermodynamic parameters such as free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$) provide key insights into the nature of the adsorption process, whether it is spontaneous, endothermic or exothermic, and the degree of randomness at the solid-liquid interface during adsorption. The thermodynamic parameters for the adsorption of arsenic using both raw and heat-treated cassava chaff were estimated using the equations below (Sahmoune 2018b; Qurrat-ul *et al*. 2020; Ademoyegun *et al.* 2022; Li *et al*. 2022),

$$K_d = {}^{q_e}/_{C_e} \tag{9}$$

$$\ln K_d = {}^{\Delta S^o}/_{R} - {}^{\Delta H^o}/_{RT} \tag{10}$$

$$\Delta G^o = RTlnK_d \tag{11}$$

where K_d denotes the distribution coefficient of the adsorption in L/g, q_e and C_e have been previously defined, and T stands for the absolute temperature in K. The plot of InK_d *versus* the reciprocal of temperature is shown in Fig. 11, which was used to determine the thermodynamic constants as listed in Table 4. Both raw and heat-treated cassava chaff showed negative Δ*G*° values, indicating that the adsorption of arsenic onto the cassava chaff was spontaneous at all temperatures studied (Li *et al*. 2022). For raw cassava chaff, Δ*G*° became more negative with increasing temperature, from -0.12 kJ/mol at 298 K to -1.24 kJ/mol at 338 K, suggesting that the spontaneity of adsorption improves at higher temperatures. Similarly, for heat-treated cassava chaff, the Δ*G*° values also became more negative with increasing temperature, but the overall change was slightly less dramatic, from -0.22 kJ/mol at 298 K to -1.19 kJ/mol at 338 K. This suggests that the adsorption remained spontaneous but with a smaller increase in spontaneity compared to the raw sample. In terms of magnitude, the heat-treated cassava chaff showed a slightly higher spontaneity at lower temperatures (298 K) compared to the raw sample, but the raw cassava chaff exhibited higher spontaneity at elevated temperatures (338 K). Sugarcane bagasse (SCB), an inexpensive agro-waste byproduct, was explored by Gupta *et al.* (2015) for its effectiveness in removing As(III) and As(V) an thermodynamic analysis indicated that the adsorption process for both As species was spontaneous and endothermic.

Table 4. Thermodynamic Variables for the Adsorption of As by Raw and Heat-Treated Cassava Chaff

***T* (K)**	Δ ***G*** kJ/mol	Δ ***H*** kJ/mol	Δ ***S*** J/mol·K	Δ ***G*** kJ/mol	Δ ***H*** kJ/molkJ/mol	Δ ***S*** J /mol·K
	Heat-treated Cassava Chaff			Raw Cassava Chaff		
298	-0.22			-0.12		
303	-0.58			-0.16		
308	-0.87	35.27	15.88	-0.19	55.27	21.37
313	-1.04			-1.03		
318	-1.08			-1.07		
328	-1.13			-1.2		
338	-1.19			-1.24		

From the study of the enthalpy change, both raw and heat-treated cassava chaff exhibited positive Δ*H*° values, confirming that the adsorption of As is an endothermic process (Sahmoune 2018b; Ogundiran *et al*. 2022). However, the enthalpy change for heat-treated cassava chaff was less, at +35.27 kJ/mol, compared to +55.27 kJ/mol for the raw sample, and this suggests that the raw cassava chaff required more energy to adsorb arsenic. The higher Δ*H*° for the heat-treated chaff also indicates that it may be better suited for adsorption at elevated temperatures, as it can benefit more from the absorption of heat.

Both raw and heat-treated cassava chaff had positive Δ*S*° values, indicating an increase in disorder at the solid-liquid interface during As adsorption (Ofudje *et al*. 2020a; Li *et al*. 2022). This increase in entropy suggests that the arsenic molecules were more freely dispersed when interacting with the surface of the cassava chaff, contributing to a more favorable adsorption process. Furthermore, the raw cassava chaff exhibited a higher entropy change (+21.4 J/mol·K) compared to the raw sample (+15.6 J/mol·K). This is because during the adsorption process, the raw cassava chaff requires more heat to adsorb possibly due to smaller surface area or less active sites on the raw material.

Desorption Study

The results on the desorption of As using raw and heat-treated cassava chaff demonstrate how the reusability of the adsorbent materials declined over multiple cycles of use, as shown in Fig. 12. These findings provide valuable information regarding the durability and long-term efficiency of cassava chaff, both raw and heat-treated, as adsorbents for arsenic. For raw cassava chaff, the percentage adsorption declined from 65.4% in the first cycle to 52.8% by the fifth cycle, but for heat-treated cassava chaff, the percentage adsorption declined from 74.2% in the first cycle to 59.0% by the fifth cycle. After five cycles, reductions in adsorption capacity (from 65.4% to 52.8% for raw chaff, and from 74.2% to 59.0% for heat-treated chaff) but this reduction was less within the first three cycles of operations, indicating that both materials can be subject to reusability after each adsorption experiment. The heat treatment of the cassava chaff consistently showed higher adsorption percentages compared to raw chaff across all cycles. In the first cycle, the heat-treated sample achieved 74.2% adsorption, which was much higher than the 65.4% of raw chaff. Even by the fifth cycle, heat-treated chaff still maintained 59.0% adsorption, while raw chaff dropped to 52.8%. This indicates that heat treatment enhances the reusability of cassava chaff, allowing it to retain more of its adsorption efficiency over multiple cycles compared to the raw form.

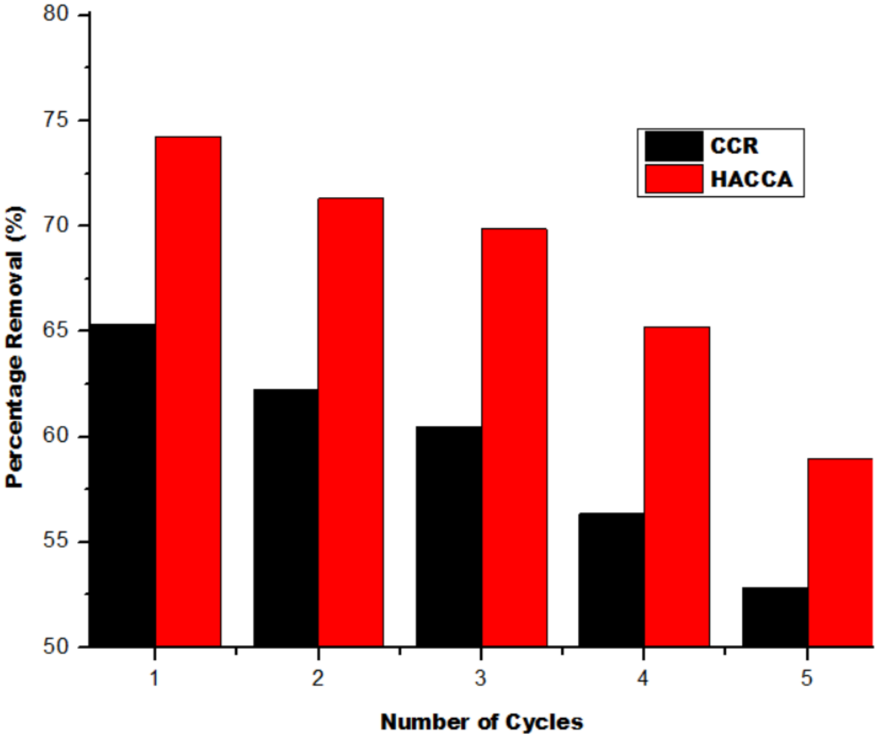


Fig. 12. Plots of percentage removal against number of cycles

During the regeneration of the adsorbent, arsenic is desorbed into an aqueous solution, requiring proper treatment to prevent environmental contamination. During this process, arsenate ion could be recovered *via* multiple washing cycles or stronger desorbing agents. Another means of ensuring that As is not left in solution is the use of chemical precipitation, where ferric salts or lime convert arsenic into insoluble arsenates, allowing for solid residue separation and safe disposal. Through the use of chelating agents like EDTA, or citrate, As ions present in the solution can form complexes with metal-arsenate interactions.

Mechanism of the Adsorption Process

The Langmuir model points to a monolayer adsorption process with a relatively uniform distribution of adsorption sites on the heat-treated cassava chaff surface. In contrast, the Freundlich model suggests that the adsorption occurs on a heterogeneous surface, with varying energies and the possibility of multilayer adsorption, and is ideal for the raw cassava chaff. Given the higher R^2 value for the Langmuir model, it seems that heat treatment may enhance the homogeneity of the surface to some extent. The zero point charge (pH_{ZPC}) of cassava biochar obtained was 5.0 and 5.4 for CCR and HACCA respectively at pH lower than the pH_{ZPC}, the biochar surface is said to be positively charged, but with pH above pH_{ZPC}, the solid adsorbent surface of the adsorbent is negatively charged (Chowdhury and Yanful 2010; Attinti *et al.* 2013). On the strength of the zero-point charge obtained in this current study, cassava chaff surfaces were positively charged at pH below 5.0 for CCR or 5.4 for HACCA and this positive charge surface enhanced the attraction of the As(V) anions, that led to higher amount of uptake at acidic pH. In contrast, cassava chaff's surface becomes negatively charged at pH above 5.0 or 5.4, which led to electrostatic repulsion between the anionic As(V) and the negatively charged adsorbent surface. This implies that the main mechanism for the adsorption of As(V) by cassava chaff from this study is electrostatic attraction.

PROPOSED MECHANISM

The interaction mechanisms between cassava chaff ash and arsenic ions during adsorption could be controlled by several mechanisms due to the rich nature of the adsorbent and the ability of arsenic ions to exist in different forms under different pH conditions. First the various functional groups on the cassava chaff ash surface, such as carboxyl (-COOH) groups, can exchange their cations with arsenic ions (As^{3+} or AsO_4^{3-}) present in the aqueous solution and leading to ion exchange mechanism (Babu *et al*. 2022; Mojiri *et al*. 2024).

At pH of 4.5, which was obtained as the optimum value in this study, the surface of cassava chaff ash tends to acquire a positive charge, and this can get attracted to arsenic species in water, particularly arsenate (AsO_4^{3-}) or arsenite (AsO_2^-) ions through electrostatic attraction mechanism as described schematically below:

$$\text{R-Surface}^+ + AsO_4^{3-} \rightarrow \text{R-Surface}^+ ... AsO_4^{3-} \quad (12)$$

Moreover, arsenic ions can form stable complexes with functional groups on the cassava ash surface, such as hydroxyls, through coordination bonds resulting in the formation of chemical complexes.

LIMITATIONS AND FUTURE DIRECTIONS

One of the major limitations for the study based on the findings provided is the use of batch process, which does not fully replicate the dynamics of continuous systems often used in real-world applications. Results from batch studies may not translate directly to column or industrial-scale processes. Also, the adsorption efficiency showed significant dependence on pH, with optimal performance at approximately 4.5. This narrow optimal range may limit practical applications, as water sources often vary widely in pH. Similarly, scaling up production of cassava chaff ash could lead to large quantities of ash, which may pose disposal challenges if not managed properly. The composition of the ash must be monitored to prevent leaching of harmful elements into treated water or the environment. Finally, heat treatment of cassava chaff requires energy, and it could contribute to cost of production. Future research could explore the use of cassava chaff in continuous flow systems, such as fixed-bed columns, to better simulate real-world applications and provide insights into breakthrough curves and operational stability. Also, adopting methods to investigate a widen pH range of adsorption, such as surface modification (*e.g.*, acid/base treatment or impregnation with metal oxides) is suggested for future prospect. The use of renewable energy sources for the ash preparation could be explored in future study.

CONCLUSIONS

In this study raw and heat-treated cassava chaff were deployed for eliminating arsenic ions from an aqueous solution.

1. The results demonstrated that temperature, dosage, contact time, and pH play crucial roles in determining the adsorption efficiency of As on raw cassava chaff.
2. By demonstrating its effectiveness, particularly in heat-treated form, the work contributes to addressing the global need for accessible water treatment solutions, especially in developing regions.
3. The endothermic nature of adsorption, compatibility with acidic to neutral pH levels, and insights into adsorption kinetics and mechanisms underline its practical applicability.
4. However, limitations include reduced adsorption efficiency at extreme pH levels and potential desorption under alkaline conditions, along with challenges posed by temperature fluctuations in diverse climates.
5. Future research should focus on optimizing cassava chaff ash through surface modifications, enhancing its stability in varying environmental conditions, and evaluating its performance in real-world water systems with competing ions.

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Conflict of Interest

No conflict of interest exists.

Data Availability

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

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