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# Removal of Heavy Metals from Oil-Well Produced Water Using Agriculture Waste as Adsorbent

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***ABSTRACT***
*Your project presents an innovative approach for utilizing cassava stem biochar (CSB) as an effective adsorbent for removing heavy metals from oil-well produced water. The key steps involved include carbonizing cassava stem at 350°C in a muffle furnace for 3 hours and 30 minutes to produce biochar, which is then tested through batch adsorption experiments. The study specifically highlights the removal efficiency for metals like boron (B), chromium (Cr), silicon (Si), copper (Cu), and iron (Fe), achieving up to 91% removal in the case of boron. Notably, an adsorbent dosage of 2.5 g per 100 ml of produced water was optimal for most metals, though iron was removed more effectively with a lower dosage of 1.5 g.*
*These findings emphasize the potential of agricultural waste, particularly cassava stem biochar, as a sustainable and cost-effective solution for treating industrial wastewater, such as produced water from oil extraction, by mitigating the environmental impact of heavy metal contamination.*
***Keywords**: Cassava stem biochar (CSB), heavy metal removal, adsorption, oil-well produced water, agricultural waste.*

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## I. INTRODUCTION

Industrial activities, particularly oil and gas extraction, generate significant volumes of produced water that often contain toxic heavy metals such as chromium (Cr), boron (B), silicon (Si), copper (Cu), and iron (Fe). These contaminants, if improperly managed, can pose serious environmental and health risks due to their persistence and potential for bioaccumulation in ecosystems. Conventional treatment methods for removing heavy metals from wastewater can be costly and environmentally unsustainable, driving the need for more affordable and eco-friendly alternatives.

One promising approach is the use of agricultural waste materials as adsorbents. Cassava stems, a byproduct of cassava farming, offer a sustainable resource for producing biochar, an effective adsorbent known for its porous structure and high surface area, which enhances its metal-binding capacity. By converting cassava stems into biochar through a carbonization process, this research explores the potential of cassava stem biochar (CSB) as a low-cost, effective adsorbent for removing heavy metals from oil-well produced water.

This study aims to evaluate the efficiency of CSB in the adsorption of heavy metals, examining parameters such as adsorbent dosage to optimize the removal of Cr, B, Si, Cu, and Fe from produced water. The results of this research could contribute to more sustainable waste management practices by repurposing agricultural byproducts for environmental remediation, particularly in the context of produced water treatment in the oil and gas sector.

Several methods are employed to treat produced water, each with its advantages, limitations, and suitability based on the specific composition and contaminants in the water. Here's an overview of common treatment methods for produced water, with a focus on removing contaminants like heavy metals, salts, and hydrocarbons.

Physical Treatment Methods

Filtration: Used for removing suspended solids and particles through physical barriers like sand filters, membrane filters, and cartridge filters. Microfiltration and ultrafiltration are common in produced water treatment, especially for pre-treatment before other processes.

Gravity Separation: Includes techniques like skimming and sedimentation, which separate oil and water based on density differences. It is a primary treatment step for produced water to remove bulk oil content.

Flotation: Dissolved air flotation (DAF) is widely used to remove oil and suspended solids. Fine air bubbles are injected into the water, attaching to oil droplets and particles, allowing them to float to the surface for removal.

Electrocoagulation: Uses an electric current to induce coagulation, helping to agglomerate contaminants into larger particles that can be separated. This method is effective for removing oil, suspended solids, and some heavy metals.

Chemical Treatment Methods

Chemical Precipitation: Involves adding chemicals like lime, sodium hydroxide, or coagulants to precipitate heavy metals and salts out of the water. It's particularly effective for reducing metal concentrations, though it can generate sludge that requires further disposal.

Oxidation and Reduction: Chemicals like chlorine, ozone, or hydrogen peroxide are used to oxidize organic contaminants and some metals. Oxidative treatments can reduce the concentration of certain metals and break down organic contaminants, though it may require subsequent steps to remove oxidation by-products.

pH Adjustment: Adjusting pH can help remove certain heavy metals and other contaminants by making them precipitate out of solution. It is often used in combination with other chemical treatments to optimize their efficacy.

Surfactant Addition: Surfactants are sometimes used to break oil-water emulsions, making it easier to separate oil from water. This can be useful for water containing stable emulsions.

Biological Treatment Methods

Aerobic and Anaerobic Treatment: Microbial processes can break down organic contaminants, including hydrocarbons, under aerobic (oxygen-rich) or anaerobic (oxygen-free) conditions. Biological treatments are effective for biodegradable organic matter but may be limited in removing metals and salts.

Constructed Wetlands: Natural or engineered wetlands are used to treat produced water by using plants, soil, and microbes to adsorb and degrade contaminants. They are low-cost but require space and may not be suitable for highly contaminated or saline produced water.

Bioreactors: Advanced bioreactors, such as membrane bioreactors (MBRs), can enhance microbial activity and improve the efficiency of contaminant degradation. MBRs combine biological treatment with membrane filtration, providing high removal efficiency for organic contaminants.

Membrane-Based Treatment Methods

Reverse Osmosis (RO): An effective method for desalination and removing dissolved salts, ions, and metals. It forces water through a semi-permeable membrane, leaving contaminants behind. RO is effective but can be energy-intensive and may suffer from membrane fouling.

Nanofiltration (NF) and Ultrafiltration (UF): Both use pressure-driven membranes to separate contaminants based on size. NF removes divalent ions and some larger molecules, while UF is effective for removing suspended solids, oil droplets, and some large organic molecules.

Electrodialysis (ED) and Electrodialysis Reversal (EDR): These electrochemical processes use electrical potential to drive ion separation through selective membranes. They are used to reduce salinity in produced water, especially where high total dissolved solids (TDS) concentrations are present.

Adsorption-Based Methods

Activated Carbon Adsorption: Commonly used for removing organic contaminants and some heavy metals. Activated carbon has a high surface area and is effective at adsorbing a wide range of contaminants, though it may be costly for high-volume applications.

Biochar and Agricultural Waste Adsorbents: Emerging research has shown that biochar from agricultural waste (like cassava stems, coconut shells, or rice husk) can effectively adsorb heavy metals and some organics. This method is sustainable and cost-effective, though it may require optimization for specific contaminant types.

Zeolites and Clays: Natural adsorbents like zeolites and clay minerals can effectively adsorb metals and some organic compounds. They offer a low-cost alternative to activated carbon but may require large quantities for high-efficiency removal.

Advanced Oxidation Processes (AOPs)

Ozonation: Ozone is used to oxidize organic contaminants, breaking them down into simpler, less harmful compounds. It's effective but requires controlled conditions and can produce harmful by-products if not managed properly.

Fenton and Photo-Fenton Processes: Involves the use of hydrogen peroxide and iron catalysts to produce hydroxyl radicals, which can oxidize a wide range of organic pollutants. The process is effective for organic contaminants, though not ideal for removing heavy metals.

Ultraviolet (UV) Treatment: UV radiation can degrade organic pollutants and, when combined with oxidants like $H_2O_2$, enhances the degradation efficiency. This method is useful for disinfection and organic breakdown, though it doesn't directly target metals.

Each treatment method has specific strengths and limitations depending on the composition of the produced water and the contaminants targeted. For example, physical separation methods like flotation and gravity separation are effective for oil removal, while membrane filtration and adsorption are more efficient for dissolved metals and salts. Increasingly, combined treatment approaches (such as adsorption followed by membrane filtration) are used to optimize efficiency, reduce costs, and meet environmental discharge standards.

The treatment of produced water from oil and gas extraction has become a critical environmental challenge, particularly due to the high concentrations of heavy metals like chromium (Cr), boron (B), silicon (Si), copper (Cu), and iron (Fe) commonly present. Heavy metals in produced water pose significant risks due to their toxicity, persistence, and potential to bioaccumulate in ecosystems. The environmental and public health impacts associated with heavy metal contamination underscore the need for effective removal methods.

Traditional methods for removing heavy metals from wastewater include chemical precipitation, ion exchange, membrane filtration, and coagulation/flocculation. However, these methods are often costly, energy-intensive, and may produce secondary pollutants. Thus, there is a growing interest in developing alternative, sustainable solutions that leverage low-cost, renewable resources. One such approach is the use of biochar derived from agricultural waste as an adsorbent, which has been shown to be effective in removing various contaminants from water.

Biochar is a carbon-rich material produced through the thermal decomposition of biomass under low or no oxygen conditions (pyrolysis). Its high porosity, large surface area, and functional groups make it an excellent candidate for adsorbing heavy metals. Various studies have demonstrated the efficacy of biochar derived from agricultural wastes, such as rice husks, coconut shells, and bamboo, in removing metals like lead (Pb), cadmium (Cd), zinc (Zn), and copper (Cu) from aqueous solutions.

The adsorption capacity of biochar can vary depending on the feedstock type, pyrolysis temperature, and activation methods. Studies have found that biochars produced at moderate temperatures (300–500°C) often exhibit optimal adsorption capacities for heavy metals due to the balanced development of porosity and surface functional groups. Additionally, the presence of oxygenated functional groups on biochar surfaces, such as hydroxyl, carboxyl, and carbonyl groups, enhances the adsorption of metal ions through mechanisms like ion exchange, complexation, and electrostatic interactions.

Agricultural waste materials present a valuable and sustainable source of feedstock for biochar production. Cassava (Manihot esculenta) is one of the most widely cultivated crops in tropical regions, producing large amounts of agricultural residues such as cassava stems. These stems are typically discarded or burned, contributing to environmental waste and greenhouse gas emissions. Repurposing cassava stems as a biochar feedstock offers a twofold environmental benefit by managing agricultural waste and providing a cost-effective adsorbent for water treatment.

Research on cassava stem biochar (CSB) as an adsorbent is limited, but preliminary studies suggest that CSB has favorable structural properties that enhance its capacity to adsorb heavy metals. The effectiveness of CSB in adsorbing metals such as cadmium, lead, and copper has been demonstrated in previous studies, but limited research specifically targets its use in treating oil-well produced water. By exploring CSB for this purpose, the current study aims to fill a gap in the literature and offer an innovative solution to heavy metal pollution in produced water.

Heavy metal adsorption onto biochar generally occurs through various mechanisms, including ion exchange, surface complexation, precipitation, and electrostatic interactions. Each heavy metal exhibits different affinities to biochar depending on factors like pH, temperature, and biochar properties. Chromium (Cr), for example, is known for its redox sensitivity and often exists in multiple oxidation states, which influences its interaction with biochar. Iron (Fe) can also adsorb effectively due to electrostatic attraction and surface precipitation.

Biochar dosage and particle size are important parameters influencing adsorption efficiency. Studies have shown that increasing biochar dosage generally improves metal removal, although adsorption efficiency may plateau beyond a certain dosage. Additionally, the particle size and surface area of biochar influence the exposure of adsorption sites, thereby affecting adsorption rates.

Produced water is a complex mixture of hydrocarbons, salts, and heavy metals, which makes it challenging to treat with conventional methods. Recent studies have begun exploring biochar as a potential solution, with promising results. For instance, biochar derived from rice husk and other agricultural residues has shown significant removal efficiencies for heavy metals in produced water, demonstrating that biochar can be an effective medium for adsorption-based treatment methods. However, few studies have investigated biochars derived from cassava stems specifically for produced water treatment, highlighting a key research gap that this study seeks to address.

While the application of biochar for heavy metal removal is well-documented, research on cassava stem biochar (CSB) for treating oil-well produced water is sparse. Moreover, understanding the specific adsorption mechanisms and optimal conditions for heavy metal removal using CSB remains limited. This study aims to bridge these gaps by evaluating the performance of CSB in removing Cr, B, Si, Cu, and Fe from produced water, with a focus on optimizing adsorbent dosage and exploring adsorption mechanisms. The findings from this research could contribute valuable insights into the application of agricultural waste-based biochar in industrial wastewater treatment, promoting more sustainable practices in the oil and gas industry.

## II. MATERIALS AND METHODS

Materials

Cassava Stem: The primary feedstock for biochar production was obtained from local agricultural sources. The cassava stems were cleaned, air-dried, and cut into smaller pieces before carbonization.

Chemicals and Reagents: Analytical-grade chemicals, including hydrochloric acid (HCl) and sodium hydroxide (NaOH), were used for pH adjustment of the produced water. Deionized water was used for solution preparation and washing.

Produced Water Samples: Samples of produced water, containing known concentrations of heavy metals such as chromium (Cr), boron (B), silicon (Si), copper (Cu), and iron (Fe), were obtained from an oil production site. The samples were characterized to determine the initial concentrations of these metals before treatment.

Preparation of Cassava Stem Biochar (CSB)

The biochar was prepared by following these steps:

Pre-Treatment of Cassava Stem: The cassava stems were washed with deionized water to remove any dirt or impurities and then air-dried. After drying, the stems were cut into smaller pieces (approximately 2–3 cm) to facilitate carbonization.

Carbonization Process: The prepared cassava stem pieces were subjected to carbonization in a muffle furnace at a temperature of 350°C for 3 hours and 30 minutes. The carbonization process was conducted under limited oxygen conditions to convert the cassava stems into biochar.

Grinding and Sieving: After cooling, the carbonized cassava stems were ground and sieved to obtain a uniform particle size (approximately 0.5–1.0 mm) to enhance adsorption efficiency. The biochar was stored in an airtight container for subsequent use.

Characterization of Biochar

Surface Area and Porosity: The specific surface area and porosity of the biochar were determined using BET (Brunauer-Emmett-Teller) analysis to assess its suitability as an adsorbent.

pH and Moisture Content: The pH of the biochar was measured in a deionized water suspension to determine its initial acidity or alkalinity. Moisture content was determined by drying a known mass of biochar and calculating the weight loss.

Functional Group Analysis: Fourier Transform Infrared (FTIR) spectroscopy was performed to identify functional groups present on the biochar surface, such as hydroxyl, carboxyl, and carbonyl groups, which are associated with metal-binding properties.

Batch Adsorption Experiments

Batch adsorption experiments were conducted to assess the effectiveness of cassava stem biochar in removing heavy metals from produced water. The experiments varied adsorbent dosage and contact time to determine optimal conditions.

Preparation of Adsorbent Dosages: Biochar samples of varying dosages (0.5, 1.0, 1.5, 2.0, and 2.5 g) were prepared for each 100 ml of produced water to identify the dosage that maximized metal removal.

Adsorption Procedure:

Metal Removal: Each biochar sample was added to 100 ml of produced water in separate 250 ml Erlenmeyer flasks.

Contact Time: The mixtures were stirred at a constant speed (150 rpm) on a magnetic stirrer to ensure uniform contact between the biochar and produced water.

Sampling: Aliquots were collected at specific intervals (30 min, 1 hr, 2 hr, and 3 hr) to evaluate the removal efficiency over time.

Filtration and Analysis: After each experiment, the samples were filtered to remove biochar particles. The filtrates were then analyzed to determine the concentrations of Cr, B, Si, Cu, and Fe.

Analytical Methods

Heavy Metal Concentration Measurement: The concentrations of heavy metals (Cr, B, Si, Cu, and Fe) in the produced water samples were measured before and after adsorption using an Atomic Absorption Spectrophotometer (AAS) or Inductively Coupled Plasma Mass Spectrometry (ICP-MS), ensuring accurate quantification.

pH Measurement: The pH of the produced water was monitored before and after each adsorption experiment to assess any changes in water chemistry that could influence adsorption efficiency.

Calculation of Removal Efficiency: The percentage removal of each metal was calculated using the formula:

$$\text{Removal Efficiency (\%)} = [(C_i - C_f)/C_i] \times 100$$

Optimization Studies
Effect of Adsorbent Dosage: By varying the adsorbent dosages (0.5–2.5 g per 100 ml), the optimal dosage for maximum heavy metal removal was identified.
Contact Time Optimization: The effect of contact time was evaluated to determine the time required to reach equilibrium for each metal.
Isotherm and Kinetic Modeling: Adsorption isotherms (such as Langmuir and Freundlich) and kinetic models (such as pseudo-first-order and pseudo-second-order) were applied to understand the adsorption process and the mechanism by which biochar binds to metal ions.
Data Analysis
Statistical analyses were performed to evaluate the effects of adsorbent dosage and contact time on metal removal efficiency. Data analysis software was used to determine isotherm and kinetic model parameters, as well as to calculate removal efficiencies for each heavy metal under various conditions.

The methodology outlined above provides a comprehensive framework for assessing the effectiveness of cassava stem biochar as an adsorbent in removing heavy metals from oil-well produced water. This approach is intended to optimize treatment conditions, contributing to the sustainable use of agricultural waste for environmental remediation.

## III. RESULTS AND DISCUSSION

Cassava stem biochar demonstrated high removal efficiencies for chromium, boron, silicon, copper, and iron in oil-well produced water, achieving optimal results at 2.5 g adsorbent dosage. The adsorption isotherms and kinetic models suggest that the adsorption process is predominantly chemisorptive, with functional groups on the CSB surface facilitating metal binding. These findings underscore the effectiveness of agricultural waste-based biochar in industrial wastewater treatment, contributing to sustainable practices in the oil and gas sector and promoting the reuse of agricultural residues for environmental applications.

Figure 1; shows that the highest percentage of iron absorption was in sample No. 3, where the CSB was 1.5 and the removal percentage was 88.4. We also concluded that the lower the after adsorption, the higher the removal percentage

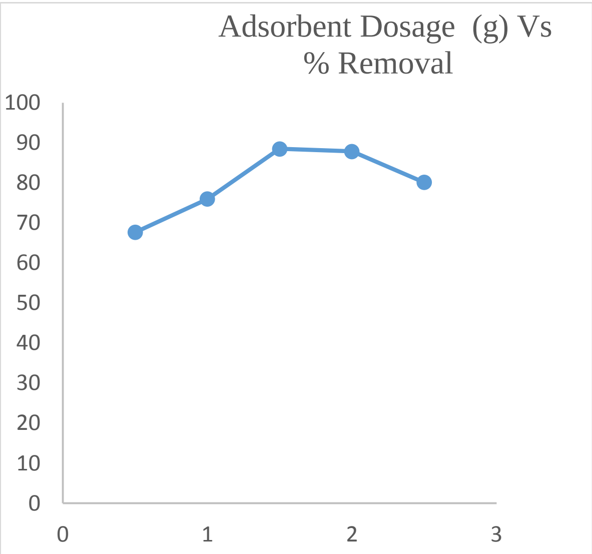


Figure 1

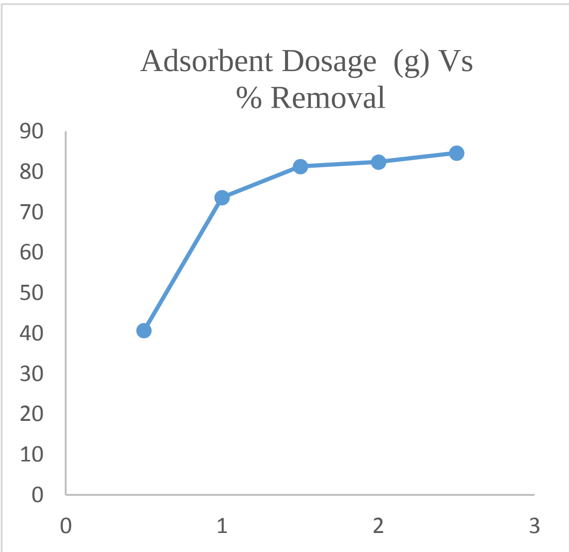


Figure 2

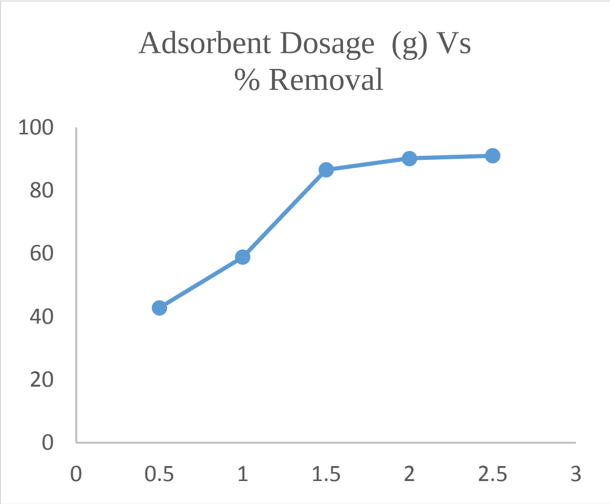


Figure 3

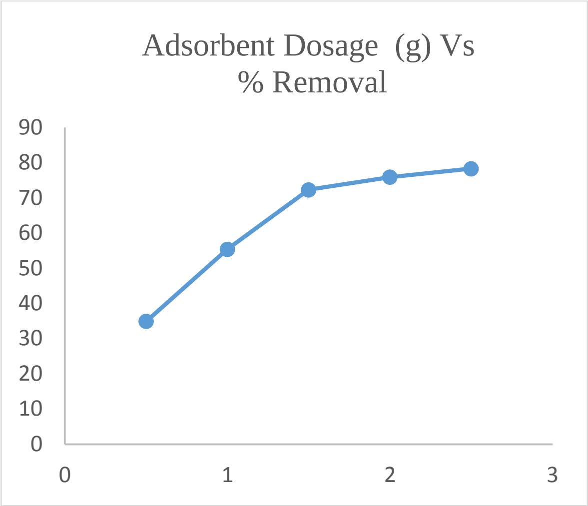


Figure 4

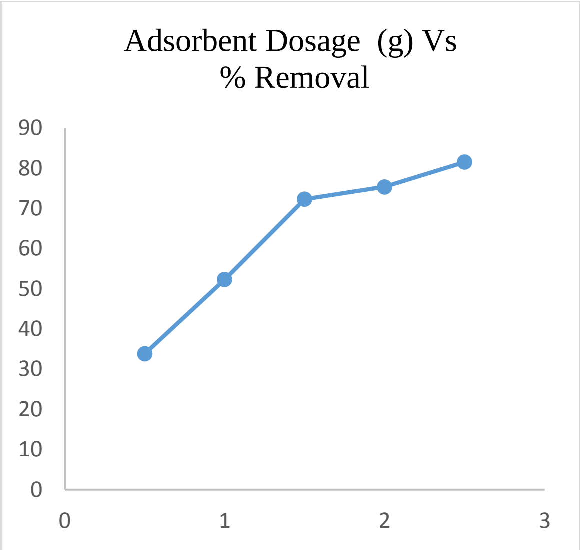


Figure 5

Copper

Figure 2, indicates that the highest percentage of copper absorption was in sample No. 5, where the CSB was 2.5 and the removal percentage was 84.6. We also concluded that the lower the after adsorption , the higher the removal percentage

Boron

Figure 3, indicates that the highest percentage of boron absorption was in sample No. 5, where the CSB was 2.5 and the removal percentage was 91.0. We also concluded that the lower the after adsorption, the higher the removal percentage.

Chromium

Figure 4, indicates that the highest percentage of chromium absorption was in sample No. 5, where the CSB was 2.5 and the removal percentage was 78.3. We also concluded that the lower the after adsorption, the higher the removal percentage

Silicon

Figure 5, indicates that the highest percentage of silicon absorption was in sample No. 5, where the CSB was 2.5 and the removal percentage was 81.5. We also concluded that the lower the after adsorption, the higher the removal percentage

## IV. CONCLUSION

In this study, we assessed the effectiveness of cassava stem biochar (CSB) for removing heavy metals from oil-well produced water. The cassava stem was transformed into biochar through carbonization at 350°C for 3 hours and 30 minutes in a muffle furnace. This biochar was then used as an adsorbent in batch adsorption experiments, with varying dosages to determine optimal conditions for maximum heavy metal removal.

The results showed high removal efficiencies for several metals: boron (B) at 91%, chromium (Cr) at 78%, silicon (Si) at 81%, copper (Cu) at 84%, and iron (Fe) at 88%. The optimum adsorbent dosage for most metals was 2.5 g per 100 ml of produced water, though iron achieved its highest removal efficiency at a dosage of 1.5 g. These results highlight cassava stem biochar's potential as a sustainable and effective adsorbent for heavy metal removal from produced water, offering a promising solution for environmental management in industrial wastewater treatment.

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