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Walnut Shell: An Effective Treatment for Cassava Wastewater

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ABSTRACT

Cassava wastewater, a byproduct of cassava processing, poses significant environmental challenges due to its high levels of organic compounds, cyanogenic glycosides, and other pollutants. This study focuses on investigating the feasibility of using walnut shell-based activated carbon as an eco-friendly and cost-effective adsorbent for removing contaminants from cassava effluents.Walnut shells were processed into activated carbon through activation and carbonization using orthophosphoric acid as the activating agent. The prepared activated carbon was then used in a column setup where the cassava wastewater was passed through the column to allow for the adsorption of contaminants. Heavy metals, COD, sulphates, nitrates, and pH analysis were carried out before and after treatment to assess the adsorbent's effectiveness. The results showed that the concentration of Cyanide reduced from 3.91 ± 0.10 mg/L to 1.91 ± 0.15 mg/L. Chromium reduced from 0.07 ± 0.01 mg/L to 0.03 ± 0.01 mg/L, Lead reduced from 11.25 ± 0.31 mg/L to 0.97 ± 0.06 mg/L, while cadmium and manganese were completely removed from the effluent. A slight change was observed in the COD level. Sulphate levels decreased from 677.00 ± 4.00 mg/L to 178.48 ± 0.54 mg/L, while nitrate concentrations dropped from 54.40 ± 0.40 mg/L to 21.27 ± 0.78 mg/L. The findings in this study affirmed that walnut shell-based activated carbon is an effective adsorbent for the treatment of cassava wastewater.

KEYWORDS: Contaminants, Adsorption, Pollutants, Effluent, Cassava.

1. INTRODUCTION

Cassava (Manihot esculenta) is one of the most important crops in many tropical and subtropical regions, with its processing being a significant source of economic activity.Although cassava plays a significant role in both the food and industrial sectors, its processing into starch involves procedures that generate substantial amounts of waste. The primary by-product of this process is cassava-washing water, also known as manipueira.[1]However, this effluent contains high levels of organic pollutants, suspended solids, and cyanogenic compounds, all of which are harmful to the environment. Research indicates that cassava factory effluent contains high biochemical oxygen demand (BOD) and chemical oxygen demand (COD), leading to oxygen depletion in water bodies.[2]If not properly managed, the discharge of this effluent into the environment can lead to severe pollution issues. This is primarily due to its high organic content and the presence of cyanide, a toxic substance harmful to most aerobic organisms, produced through the hydrolysis of cyanogenic glycosides naturally found in cassava tubers.[3]This effluent can cause environmental pollution, water contamination, and aquatic ecosystem disruption among others.

Chemical treatments, such as coagulation and precipitation, may help remove some contaminants but require costly chemicals and infrastructure that may be unavailable or unaffordable in rural areas where cassava processing is most common. Biological treatments, while capable of degrading organic matter, are not always effective at breaking down cyanogenic compounds, leaving hazardous toxins in the water. Furthermore, physical treatments, such as filtration and sedimentation, do not fully address the removal of dissolved organic and toxic compounds, thus limiting their overall effectiveness.[4]

There is a growing need for sustainable and environmentally friendly alternatives that make use of natural waste products. Among the various techniques employed for the removal of chemical contaminants from the environment such as electrochemical reactions, membrane separation, anaerobic and aerobic biodegradation, and advanced oxidation processes, adsorption stands out as one of the most widely adopted methods. Its widespread application can be attributed to several advantages, including low energy requirements, environmental friendliness, high adsorption capacity, favorable surface morphology, and reusability.[5-6]Walnut shells, a byproduct of walnut processing, have attracted attention due to their high lignocellulosic content and excellent adsorption properties. They

are widely available, low-cost, and offer a greener solution for wastewater treatment,[7] which is an indication of a good precursor for the adsorptive treatment of cassava wastewater.

The purpose of this study is to explore the potential of walnut shells as a natural adsorbent for the treatment and purification of wastewater originating from cassava processing plants, with the objective of minimizing the concentration of organic pollutants and cyanogenic compounds in the resulting effluent.

2. MATERIALS AND METHODS

2.1 Chemicals used and sample collection.

The chemicals employed for this study includes: Dilute Hydrochloric (HCl) acid, Orthophosphoric acid. The chemicals are analytical grade. Walnut shell were collected from Sabo market, Ogbomoso, Oyo state, Nigeria. The cassava wastewater was collected at Aranda, Ogbomoso.

2.2 Pre-treatment and chemical activation of walnut shell-based activated carbon

Walnut shells were washed with distilled water, air-dried, ground, and sieved before being stored for adsorption studies. For activation, 300 g of sieved shell was mixed with 0.3 M orthophosphoric acid and heated with continuous stirring until fully absorbed. The mixture was cooled, then carbonized at 200 °C for 6 hours. The carbonized product was washed to neutrality with distilled water and oven-dried at 105 °C. The resulting activated carbon was stored in an air-tight container for further use.

2.3 Analysis of Raw Cassava Effluent Physicochemical parameters determination

The biological oxygen demand determination of the Cassava wastewater in mg/L was carried out using standard methods described in the guide manualAPHA[8]. The dissolved oxygen content was determined before and after incubation. Sample incubation was for 5 days at 20ºC in a BOD bottle, and physicochemical determination of the Cassava wastewater was calculated after the incubation period. The chemical oxygen demand was carried out using a Liebig condenser with a 300 mm jacket.

Elemental analysis

The mineral content of the water samples was determined using wet digestion methods as described by Aremu *et al.*[9] The process involved accurately measuring a specific amount of the sample and subjecting it to wet digestion to break down the organic matrix and release the minerals into a solution. Approximately 100 mL of the water sample was measured and placed into a clean, dry digestion flask. To the digestion flask, 10 mL of concentrated nitric acid (HNO_3) was added. This acid is a strong oxidizing agent that facilitates the breakdown of organic matter. The flasks were then placed on a hot plate or in a digestion block, and the temperature was gradually increased to approximately 150 °C. The samples were heated until the solution became clear, indicating complete digestion. After digestion, the samples were allowed to cool to room temperature. The clear digest was then diluted to 50 mL with deionized water. The concentrations of Lead, cadmium, mercury chromium and magnesium in the digested samples were determined using a flame photometer (Model 405, Corning UK).Sulphate test was performed gravimetrically and compared with spectrophotometer analysis. Nitrate and cyanide tests were performed volumetrically, and spectrophotometric analysis was done.[10]

2.4 Experimental Procedure

Cassava wastewater was treated using a column process setup of beds filled with walnut shell-derived activated carbon, chosen for its simplicity, efficiency, and capacity for large volumes. Wastewater was pumped through the column at a controlled flow rate, enabling effective contact and adsorption of organic pollutants, heavy metals, and cyanogenic compounds. Contact time was optimized to maximize adsorption. Samples were collected periodically to monitor pollutant concentrations and analyze changes in physicochemical properties, including COD, BOD, hydrogen cyanide, and heavy metals. Treatment efficiency was assessed based on the percentage removal of these contaminants, demonstrating the effectiveness of walnut shell-based activated carbon.

3. RESULTS AND DISCUSSION

The pH of a water sample is a crucial parameter that affects its overall chemical balance and influences the behavior of various pollutants and treatment efficacy.[11]For the raw water sample (RWS), the pH was 4.50±0.50, which is acidic as shown in Table 1. After treatment with walnut shell, the pH slightly reduced to 4.10±0.24. Although this change is minimal, it suggests that walnut shells do not significantly alter the pH. In general, pH can be affected by adsorbents, particularly those that release acidic or basic components.[12] However, walnut shells, being a natural organic adsorbent, are primarily neutral in their impact on pH levels. Literature shows that organic adsorbents, like walnut shells, have little to no significant effect on the pH, as they lack strong acidic or basic groups that could drastically change the solution's hydrogen ion concentration.[7]

Table 1: Result of physicochemical parameters and metal ion analysis on the samples

Parameters and Metal ions present	RWS	TWS	Standard (WHO) (mg/L)	EU Standard (mg/L)
pH	4.50±0.50	4.10±0.24	-	-
COD (mg/L)	212.80±0.27	162.45±0.50	< 10	-
Cadmium (mg/L)	0.03±0.01	-	0.003	0.005
Chromium (mg/L)	0.07±0.01	0.03±0.01	0.05	0.05
Manganese(mg/L)	0.04±0.01	-	0.5	0.05
Lead (mg/L)	11.25±0.31	0.97±0.06	0.01	0.01
Sulphate (mg/L)	677.00±4.00	178.48±0.54	500	250
Nitrate (mg/L)	54.40±0.40	21.27±0.78	50	50
Cyanide (mg/L)	3.91±0.10	1.91±0.15	0.07	0.05

The COD is an indicator of the organic pollutant load in wastewater. It decreased from 212.80±0.27 mg/L in the raw wastewater sample (RWS) to 162.45±0.50mg/L in the treated wastewater sample (TWS) as presented in Table 1. This reduction demonstrates the adsorbent's ability to remove organic contaminants. However, the COD value remained well above the World Health Organization (WHO) permissible limit of <10 mg/L for drinking water.[13] This suggests that while walnut shell activated carbon reduces the organic load, additional treatment steps are necessary to meet stringent standards.

Heavy metal concentrations,particularly cadmium, chromium, manganese, lead, and cyanide, exceed permissible limits in several cases. Cyanide, a highly toxic compound linked to industrial waste, was present in the raw effluent at a concentration of 3.91 ± 0.10 mg/L, which is significantly above safe levels. Treatment with walnut shell reduced this concentration by nearly 50% to 1.91 ± 0.15 mg/L. Cadmium (0.03 ± 0.01 mg/L) was completely removed after treatment, addressing concerns over its bioaccumulative and long-term health effects.[14] Lead levels decreased from 0.05 ± 0.01 mg/L to 0.01 ± 0.01 mg/L, highlighting walnut shell's strong potential for lead removal. Chromium was reduced from 0.07 ± 0.01 mg/L to 0.03 ± 0.01 mg/L, indicating partial adsorption, likely dependent on the chromium species present. Manganese, initially at 0.04 ± 0.01 mg/L, was fully eliminated, improving water quality. Sulphate concentration dropped from 677.00 ± 4.00 mg/L to 178.48 ± 0.54 mg/L, and nitrate levels decreased from 54.40 ± 0.40 mg/L to 21.27 ± 0.78 mg/L—a 60% reduction—demonstrating walnut shell's efficacy in mitigating various inorganic pollutants.

4. CONCLUSION

This study investigated the effectiveness of walnut shell-based activated carbon in the treatment of cassava wastewater. The results demonstrate that walnut shell-activated carbon is capable of reducing the levels of several key pollutants, including sulphate,nitrate and cyanide. The walnut shell effectively reduced heavy metals to safer levels. Cadmium and manganese were completely removed from the water, chromium was reduced from 0.07 ± 0.01 mg/L to 0.03 ± 0.01 mg/L, and lead decreased from 11.25 ± 0.31 mg/L to 0.97 ± 0.06 mg/L. These results indicate a strong adsorption affinity of walnut shells for heavy metals, making it suitable for applications where metal contamination is a concern.

CONFLICT OF INTERESTS

The authors declare no conflict of interests.

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