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Efficient Removal of Cassava Wastewater Contaminants Using Plantain Peel-Derived Activated Carbon

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Abstract: Cassava (Manihot esculenta Crantz) is largely processed for food in tropical Africa. Wastewaters are generated from cassava processing and contains toxic chemical contents that pose risks to humans, the environment, and other living organisms. According to the Food and Agriculture Organization, Nigeria is a leading cassava-producing country in the world; hence, addressing this problem is paramount and requires an approach that effectively removes the contaminants in the effluents. Therefore, this study is carried out to explore the removal of contaminants present in cassava wastewater. Activated carbon was prepared from plantain peels by carbonizing the peels with phosphoric acid via chemical activation. The untreated cassava wastewater and the treated cassava wastewater with plantain peel-activated carbon were subjected to water analysis using a multi-parameter water analyzer. Some of the physicochemical parameters that were determined include biochemical oxygen demand (BOD), Chemical oxygen demand (COD), cyanide, and total dissolved solids (TDS). The treated wastewater was observed to show low turbidity of 20.46 NTU from over 1050 NTU; likewise, the BOD, COD, and Cyanide reduced from 16.70 mg/l to 5.54 mg/l, 893.31 mg/l to 136.07 mg/l, and 1.028 mg/l to 0.4 mg/l respectively. This study has demonstrated the potential of plantain peel-derived activated carbon as a sustainable and effective solution for treating cassava wastewater. This would have significant implications for managing cassava wastewater effluents and environmental sustainability.

Keywords: Cassava wastewater; plantain peel; chemical oxygen demand; biochemical oxygen demand; activated carbon.

1. Introduction

1.1. Background of study.

The human quest to satisfy daily needs has resulted in process development, which aids in transforming raw materials into useful products. Cassava has a variety of applications in paper, alcohol, pharmaceutical, textile, and food industry [1]. Cassava is widely produced to meet human and animal needs in Nigeria (Figure 1), and its processing mostly involves peeling, cleansing, grating, and pressing to extract effluents [2]. This affluent water generated in the entire process is regarded as cassava wastewater, a major by-product in agro-industrial and domestic processes, where cassava is used to make food products like fufu, garri, chips, etc [3]. Cassava contains 30% water, and its processing generates large volumes of water, about 250L

- 600L per ton of cassava roots [4–7]. This wastewater is typically considered not useful and is discarded into the soil, flowing streams, and rivers because cassava effluent contains a significant amount of pollutants such as cyanide, heavy metals, pathogens, suspended solids, etc, which makes it harmful for further usage [8,9]. So, when disposed of untreated, it becomes a threat to the environment. Cassava is rich in starch, sugar, cyanide, enzymes, and cellulose, which are liberated throughout the processing stages from the roots, forming a central component and contributing to its thickness and organic nature [10,11]. After disposal, organic contents are degraded by living organisms, which results in a foul odor, low dissolved oxygen (DO) level, high biochemical oxygen demand (BOD), and chemical oxygen demand (COD) concentrations [5]. According to [12], the polluting potential of effluent is measured by the amount of oxygen required to break down organic substances, known as Chemical Oxygen Demand (COD), and the oxygen needed by microorganisms and enzymes to stabilize these organic materials, which is the Biochemical Oxygen Demand (BOD). In soil and water, cyanide is capable of forming complexes with metals like iron, copper, manganese, etc [13]. These complexes are often water-soluble, which enhances the potential for aquatic contamination [13,14]. When it finds its way into the human body, cyanide can combine with iron in the hemoglobin to compete with oxygen that flows in the bloodstream [7,13]. With Nigeria being the world's leading cassava producer, treating cassava wastewater before disposal becomes imperative due to environmental sustainability and concern for public health. Several scientific approaches, such as physical, chemical, and biological methods, have been explored to treat cassava wastewater and ensure the removal of pollutants from wastewater [15]. The major challenge of treating cassava wastewater is the high COD, Cyanide, and BOD concentrations. In most cases, treatments will require a highly efficient method carried out at suitable intervals, which can be energy-intensive, expensive, and rigorous. Conventional methods involve subjecting cassava wastewater to anaerobic, facultative, and aerobic ponds for treatment [4]. These methods have drawbacks such as ineffective anaerobic breakdown, requiring much space, and being costly [16]. Consequently, there's a growing need for affordable and innovative solutions, so researchers have developed a variety of approaches to comply with stricter regulatory discharge standards. Common methods include chemical precipitation, carbon adsorption, ion exchange, evaporation, nanoparticle, membrane procedures, or employing modified materials like silica, alumina, and resins [16,17,18]. Each approach has limitations, such as treatment process gaps, demanding capital and labor investments, frequent monitoring, and waste creation necessitating additional disposal measures [17]. Also, researchers have explored the use of biological agents for wastewater treatments. This involves living and non-living microorganisms to remove pollutants from industrial waste. Some studies have shown that microorganisms such as bacteria, algae, fungi, and yeasts can take up heavy metals and solid waste from wastewater [18,19]. Using processes that harness the natural ability of microorganisms to utilize essential components in wastewater as building blocks for cellular synthesis and energy sources needed for microorganisms' growth. This activity helps eliminate a wide range of pollutants, including those originating from raw materials and resulting by-products [20–22]. However, biocidal activity and enzymatic inhibition at high concentrations, economic constraints, and polluted biodegradation are reported as drawbacks [20,23]. Choosing the proper treatment method hinges on several factors, such as waste characteristics, concentration, effluent diversity, desired purification level, and economic considerations. According to the Food and Agriculture Organization Statistics (FAOSTAT), cassava wastewater is acidic, and its toxicity primarily arises from its high cyanide content, ranging between 15 - 400 ppm HCN and fresh weight [15]. The composition includes varied heavy metal contents such as iron, manganese, zinc, copper, cadmium, chromium, lead, silver, and mercury. With a notable chemical oxygen demand, ranging from 320 to 12,000 mg/L, other characteristics involve a total solids content ranging from 5600 to 6581 mg/L, along with a total hardness of 75.00 mg/L, while the conductivity measures above 1050 µS/cm [24,25]. The wastewater usually exhibits high levels of biochemical oxygen demand (BOD), substantial total dissolved solids at 799 mg/L, and a total suspended solids concentration of 789 mg/L. Within this context, the microbial composition includes distinct classes such as coliforms, total heterotrophic bacteria count, total fungi, lactic acid bacteria count, lipolytic, cellulolytic, phosphate-solubilizing, and nitrifying bacteria [9,11].

The wastewater treatment adsorption process is considered cost-efficient, simple (unit operation), widely used, and environmentally friendly [17,26,27]. Nonetheless, adsorption is also an effective means of removing pollutants and a better alternative to conventional and non-conventional wastewater treatment methods [16,28]. Adsorption is a process that defines the ability of modified materials (adsorbents) to trap molecules from liquids or gasses on their surfaces. It is a mass transfer process that results in the sorption of solutes by solid or liquid surfaces [29]. This happens because of adsorbents' special properties, such as high adsorption capacity, porous structure, high surface area, and versatility, which makes them capable of achieving high removal of contaminants from wastewater [30,31]. Various substances have been harnessed as adsorbents for different applications, such as water treatment, separation processes, catalysis, indicator systems, and desiccation. Among the commonly employed adsorbents are agricultural wastes, clay minerals, biopolymers, and nanomaterials [30-33]. Using agricultural waste for treatments offers several merits, including cost-effectiveness, ready availability, chemical stability, minimal processing, conservation, and environmental friendliness. These materials derived from agricultural waste comprise cellulose, lignin, and hemicellulose. Notably, the lignin component harbors polar functional groups like ether, aldehydes, ketones, alcohols, carboxylic acids, and phenolic groups, which significantly enhance the adsorption capabilities of these materials. Studies have covered the adoption of diverse agricultural wastes for wastewater treatment due to their carbonaceous nature. Adsorbents derived from plant residues or carbon-rich substances have exhibited notable efficacy in terms of water remediation [14,23] because activated carbon of carbonaceous substances has a high degree of porosity and large surface area. The term activated implies that the high porosity is a function of thermal decomposition and chemical modification [30].

Among low-cost and readily available agricultural and domestic wastes is plantain peel. It makes up 30%-40% of a typical plantain fruit, and approximately 13 million tons of these peels are wasted per year [34]. Usually, plantain peel is a by-product of plantain consumption, and the plantain chips industry, which is cellulosic and biodegradable, possesses effective adsorption capability for removing pollutants from wastewater. When heated at high temperatures, the cellulose breaks, increasing surface area, as pores form on its surface due to the release of internal volatile substances. There are several investigations into the use of plantain peels as a modified material for removing pollutants, such as the reduction of CO from biogas, removal of Zn (II) ions from aqueous solution, removal of chloroquine when supported with ZnO nanocomposite [33,36,37]. Activation using phosphoric acid is preferred for removing ash-forming contents and enlarging the pores of the adsorbent [33,38–40]. This research contributes to developing eco-friendly solutions that ensure the safe disposal of cassava wastewater to minimize the negative impacts on ecosystems and human health. Considering the limited educational and financial resources available to small and medium-sized processors, it becomes crucial for suggested treatment methods to be not only sustainable and uncomplicated but also maintain a high level of effectiveness while incurring minimal initial costs. A feasible green strategy entails employing a combined technique that efficiently breaks down cassava wastewater constituents, utilizing eco-friendly and cost-effective readily available waste.

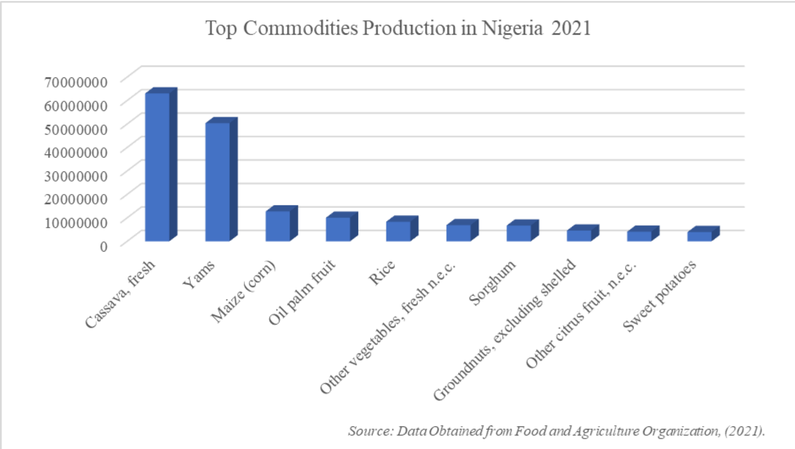

Figure 1. The leading commodities production in Nigeria for the year 2021. Cassava was the most-produced food Commodity in 2021, which suggests the level of industrial processing and wastewater generation [15].

2. Materials and Methods

2.1. Cassava wastewater.

The wastewater was collected in a plastic container at a cassava processing factory located at 8°11'45.3"N, 4°16'35.5"E Aroje, Ogbomoso to Ilorin expressway, Ogbomoso North Local Government area Oyo State, Nigeria. The plastic container was sterilized with HNO_3 and then rinsed with distilled water [41] to ensure it was pollutant-free. The pH and temperature of the wastewater were taken, and the sample was observed to be a pale-yellow liquid, thick and turbid, indicative of its inherent composition and potential chemical constituents. The collected effluent was placed in a cooler containing ice to maintain the integrity of the collected effluent and preempt any undesired photochemical reactions or deteriorations. Subsequently, the sample was taken to the laboratory, where it was stored in a controlled environment within a refrigerator, maintained at a temperature of 4°C, prior to its analysis and treatment procedures [42].

2.2. Plantain peels (Musa paradisiaca).

The Plantain peel waste used in this study was collected at Wazo Ultramodern Market Ogbomoso, located between longitude 4°15'27.61"E and latitude 8°9'56.96"N. The peels were thoroughly washed with distilled water to remove dirt and were cut into smaller sizes to hasten drying. The plantain peels were air-dried in open space to prevent the loss of lignocellulosic components of the peels that are sensitive to sunlight [44]. It took 14 days to achieve the desired texture fit for milling. Table 1 shows the proximate lignocellulosic constituents of plantain peels, indicating the adsorbent's physicochemical properties. The peels were milled to increase the surface area and achieve a composite mixture of the collected sample. The resulting powder was carbonized inside a muffle furnace at 250°C for 3 hours.

Table 1. Proximate composition, crude fibre composition, of plantain peels.

Proximate composition		**Composition of crude fiber**	
Constituents (%)		**Constituents (%)**	
Protein	8.79 ± 1.92	Cellulose	32.60
Fat	5.24 ± 2.35	Hemicellulose	46.50
Crude Fibre	32.60 ± 0.00	Lignin	25.70
Ash	22.28 ± 9.48		
Moisture	5.20 ± 2.60		
Volatile Solids	65.65 ± 0.00		

Consolidated from published data: [25,45].

2.3. Acid activation of plantain peels.

200g of Carbonized plantain peels were impregnated with 0.3 M solution of H_3PO_4 acid [45]. This immersion was allowed to proceed for 24 hours to ensure adequate time for activating surface pores. The solution was then heated using a hot plate to form a paste. The paste was introduced into a Muffle furnace preset to 500°C and maintained at this temperature for 8 hours. The activated carbon derived from plantain peel was allowed to cool to ambient temperature and thoroughly washed with distilled water to achieve an almost neutral pH as shown in Figure 2. To remove excess moisture, the wet activated sample was dried in an oven set at 100°C for 12 hours and then placed in a desiccator to facilitate cooling.

2.4. Wastewater treatment.

250 ml of cassava wastewater sample was added to 500 ml Erlenmeyer flasks at a room temperature of 25°C. 2.5 grams of the activated plantain peel was introduced to the wastewater in the flask based on solid-liquid adsorption isotherm [28].

Given as: $q = (C_w)*V/m$

Where q is the amount of adsorbate per unit mass of adsorbent, C_w (mg/l) is the concentration of adsorbate, V is the volume of the solution, and m is the mass of adsorbent.

An orbital shaker set at a rotation speed of 120 rpm was used to achieve the desired agitation. The removal process was carried out for 12 hours to have a clear solution, change in coloration, and increase pollutants deposited on the adsorbent. The mixture was made to settle and then filtered over a cotton wool. The obtained solution is the treated cassava wastewater sample that was characterized using multi-analytical machines to observe the change in parameters compared to factory effluent.

Figure 2. Images showing different stages of the wastewater treatment process.

3. Results and Discussion

The water quality parameters measured in this study provide valuable insights into the characteristics of cassava wastewater and the efficiency of wastewater treatment processes, as shown in Table 2.

Table 2. Physicochemical parameters of the treated and untreated cassava wastewater compared with World Health Organization (WHO) standard values.

Parameters	Cassava Wastewater	Cassava Wastewater + APP	WHO standard values
pH	3.47	6.92	7.0
TDS (mg/L)	573.70	460.20	500
BOD (mg/L)	16.70	5.54	5.0
COD (mg/L)	893.31	136.07	250
DO (mg/L)	1.8	7.3	6.0
Turbidity (NTU)	>1050	20.46	15
Conductivity (μS/m)	2440	1162	1200
Iron (Fe) (mg/L)	1.34	0.52	1.0
Cyanide (mg/L)	1.028	0.405	0.5
Total hardness (mg/L)	218.32	74.20	120

Legend: TDS–Total Dissolved Solids; BOD–Biochemical Oxygen Demand; COD–Chemical Oxygen Demand; DO–Dissolved Oxygen. Unit: NTU– Nephelometric Turbidity Unit; APP–Activated Plantain Peels.

The results indicate significant differences between the untreated cassava wastewater. The WHO (World Health Organization) standards are significant because they help assess the compliance of treated wastewater with regulated standards. The pH value of 3.47 in the untreated cassava wastewater is considerably acidic. According to [47], low pH can be attributed to the presence of organic acids and soluble compounds in cassava processing effluents. After treatment, a near-neutral pH of 6.92 was attained, indicating that the adsorbent successfully removed the acidic content of the wastewater. A total dissolved solids (TDS) level of 573.70 mg/L in untreated cassava wastewater reflects the high concentration of dissolved solids, including salts, organic matter, and other contaminants [48]. Compared with the WHO standard of 500 mg/L, a TDS value of 460.20 mg/L after treatment indicates the potential for safe discharge into the environment. The high BOD (16.70 mg/L) and COD (893.31 mg/L) values in the untreated cassava wastewater suggest a substantial organic pollutant load. Such high levels can deplete dissolved oxygen, adversely affecting aquatic life [49] and necessitate removal before discharge. The significant reduction in both BOD (5.54 mg/L) and COD (136.07 mg/L) after treatment demonstrates the effectiveness of the plantain peel adsorbent. Also, the change from a low DO level of 1.8 mg/L to 7.3 mg/L in treated cassava wastewater indicates the transition from a severe oxygen deficiency harmful to aquatic organisms and ecosystem health to a safer effluent supporting aquatic life [50]. The reduced total hardness value (74.20 mg/L) shows a decrease in calcium and magnesium ions concentration. This is beneficial for preventing scale formation and improving water quality [51]. The cyanide concentration stands at 1.028 mg/L, exceeding the WHO recommended guideline of 0.5 mg/L, which raises concerns about undesirable toxicity [52]. The reduction to 0.405 mg/L ensures downstream communities' safety and mitigates potential environmental impact.

Although several studies exist on the treatment of cassava wastewater, where several agricultural wastes were used, this research introduces the use of plantain peel-derived activated carbon, an underexplored material for cassava wastewater treatment. The previously published study focused on the removal of cyanide and three heavy metals, namely Lead (Pb), Chromium (Cr), and Cadmium (Cd) [53]; however, this study covers the physicochemical assessments, which are crucial and fundamental indicators of the cassava wastewater environmental impact. Moreover, according to [53], the study achieved an optimum cyanide removal efficiency of 96.45% at a contact time of 5 hours, using 15 grams of the adsorbent. With 2.5 grams of adsorbent, we achieved 60.60% cyanide removal efficiency at a contact time of 12 hours, and this proves a more resource-efficient per gram of adsorbent used, as this study employed one-sixth amount of the adsorbent used in the previous study.

4. Conclusions

The activated plantain peel is an efficient treatment material due to decreased physicochemical parameters, particularly cyanide concentration, BOD, COD, and total hardness of the treated wastewater compared with the WHO standards. Because the effluent is unfit for human use, it offers an opportunity for safe disposal of the treated wastewater into the environment without leading to soil degradation, water pollution, and loss of biodiversity. The process of using plantain peel-activated carbon to treat cassava wastewater is a low-cost technique with reduced energy costs and is eco-friendly. However, the absence of FTIR or SEM limits a comprehensive understanding of the adsorption process's structural mechanisms. Moreover, the research exclusively focused on physicochemical assessments and did not cater to the potential influence of biological factors and heavy metals, presenting an opportunity for further studies.

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Conflicts of Interest

The authors declare no conflict of interest.

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