

Mitigation of Nitrate Pollution in Wastewater: A Case Study of the Treatment of Cassava Processing Effluent Using Cassava Peel Carbon Material

Olayinka Omotosho

Abstract—The study investigated efficiency cassava peel carbon and Zinc Chloride activated cassava peel carbon at 1:3, 2:3 and 1:1 activation levels in the removal of nitrates from oxidized cassava processing wastewater. Results showed that the CPC and CPAC were effective in adsorption of nitrates. A summary of results from the study revealed that CPAC at 1:3 exhibited the highest initial decontamination (69.5% after 2 hrs) while CPAC at 1:1 activation ratio showed a slower initial decontamination rate. The CPC & CPAC exhibited Langmuir R_L values of 0.15, 0.11, 0.09, and 0.07 for the 0:1, 1:3, 2:3 and 1:1 confirming its suitability as adsorption material.

Keywords—Adsorption, Cassava, Activated Carbon, Nitrate, Isotherm, Langmuir.

I. INTRODUCTION

WATER is a resource that is unique to the earth and also crucial to the existence of life on it. Many authors have argued that access to clean water is gradually dwindling due to continuous pollution of existing water bodies. Over the last century, continued population growth and industrialization have resulted in the degradation of various ecosystems on which human life relies on [1]. Drinking water and various types of agricultural, domestic, and industrial wastewater have been known to contain several nitrogenous compounds including ammonia, nitrates, and nitrites [2].

Nitrates in particular have been known to cause severe environmental problems like eutrophication and algae boom, it has also been identified as the cause of infection diseases, such as cyanosis and cancer of the alimentary canal [3], blue baby syndrome (methemoglobinemia) in infants [4], causing mortality. Studies have shown that pollution resulting from agricultural activities can cause a significant deterioration of surface and groundwater quality. The most common pollutant types arising from it are high loads of oxygen-demanding organic compounds, associated nutrients (particularly nitrogen and phosphorus) and a variety of organic xenobiotic substances applied to cultures, soils or used in livestock, such as pesticides and pharmaceuticals [5]. Traditional methods for removal of nitrates from water include two main groups of treatment processes: biological and physicochemical. However, the physicochemical processes are the most

conventionally used and they include processes like ion exchange, reverse osmosis, electrodialysis and adsorption [6].

Cassava is one of the major food crops in many countries of the world and is ranked sixth as the most important food crop [7]. The global cassava production is currently estimated at more than 200 million tons and the trend is increasing due to higher demand for food products [8]. According to [9] most times in developing countries cassava processing industry effluent is indiscriminately disposed into adjacent flowing water bodies or on land leading to infiltration and pollution of the underground water reservoir. There is the need for wastewater from agricultural processing activities to be treated before they are discharged into the water courses or open fields in order to reduce potential environmental hazards [10], [11].

Activated carbon (AC) is one of the most popular adsorbents used in numerous industries for the removal and recovery of organic and inorganic compounds from gaseous and liquid streams [12]. Research in recent years have shown that low cost activated carbon can be produced agricultural wastes such as corn cob, rice husk, coconut shell, hazelnut bagasse, palm shell, cherry stone, cassava peels and apricot stones [13]–[20].

The study is therefore aimed at producing cassava peel carbon (CPC) and cassava peel activated carbon (CPAC) using Zinc Chloride as the activating agent in the chemical activation process. The produced CPC and CPAC would then be employed in removal of nitrate pollutant from cassava processing wastewater which has already undergone cyanide destruction process. The effects of impregnation ratio on rate of adsorption of nitrate from Hydrogen Peroxide treated cassava processing effluent investigated.

II. METHODS

A. Preparation of Cassava Peel Activated Carbon

Waste cassava (*Manihot esculenta* Crantz) peels used for the study was collected from a cassava processing industry in Ibadan, Nigeria. The cassava peels were then inspected, washed, and sundried to a moisture content of between 8–10% wet basis. The dried cassava peels were then carbonized using a muffle furnace (Carbolite, England Model AAF 11/18) at a temperature of 420°C for a period of 90 mins. Then the cassava peel carbon (CPC) was allowed to cool overnight under inert conditions thereby yielding the base carbon material (Fig. 1) for activation. The CPC size was reduced to

Olayinka Omotosho is a Research Fellow at the Institute of Agricultural Research and Training, Obafemi Awolowo University, Moor Plantation, Ibadan Oyo State, Nigeria (phone: +234-803-481-9954; e-mail: akintoshforever@gmail.com, akintoshforever@iart-ngonline.org).

500 μm . The reduced carbon was then pre-washed to remove any form of dirt that may have been attached during the size reduction process and later dried in the oven at 120°C for 8 hrs. Three samples of the CPC were activated using ZnCl_2 at activation ratios of 1:3, 2:3 and 1:1 to yield the cassava peel activated carbon (CPAC) used in the treatment process. The CPC and CPAC were then stored up in airtight glass containers (Fig. 2) to ensure the efficacy of the material is retained till when it is required for use.



Fig. 1 Cassava Peel carbon



Fig. 2 Powdered CPC and CPAC stored in airtight jars.

B. Characterization of Cassava Peel Carbon and Cassava Peel Activated Carbon

1) pH Determination

The pH value of the CPC and CPAC were determined by soaking 1g of each of the samples in 100ml of distilled water and stirred for 1 hour as recommended by [21].

2) Bulk Density

The method employed in determining the carbon materials' bulk density was the tampering procedure as described by [22].

3) Moisture Content Determination

Moisture content was determined according to ASTM 2867-99 Guidelines. 2g each of the CPC and CPAC (W) were

weighed and dried in a furnace continuously. The drying sample was constantly reweighed at a 10 mins interval until a constant weight (W_c) was obtained. The crucible and its content were retrieved and cooled in desiccators. The difference in weight (ΔW) was recorded and the moisture content (MC) calculated from (1) as loss in weight on drying divided by initial weight of carbon multiplied by 100.

$$MC = \frac{\Delta W}{W} \times 100 = \frac{2 - W_c}{2} \times 100 \quad (1)$$

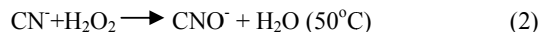
4) Pore (Void) Volume Determination

The voids volume determination for the CPC and CPAC was done following method described by [23].

C. Wastewater Treatment

Wastewater sample collected from cassava processing industry within Ibadan metropolis in opaque plastic containers and kept at a temperature of 4°C (to ensure integrity of wastewater is maintained) before transported to the laboratory.

pH of the collected waste water was taken and measured to be 4.7 it was then taken to alkaline range by the addition of 0.5M NaOH (purchased from Merck) to the wastewater until the pH was at 10. This was to ensure that the hydrogen peroxide could effectively react with substances like cyanide which could alter the result of the experiment and also prevent the release of Hydrogen cyanide gas. Hydrogen peroxide at 50% concentration was then added at a dose of 0.4 grams H_2O_2 per gram of CN^- oxidized this amounted to about 9.0 grams of hydrogen peroxide. The wastewater was then left for a period of 90 minutes to ensure a reasonable level of cyanide destruction (2).



Then the pH was then later reduced to a slightly acidic range of 5 by adding 1 Molar HCl and left to stand for another 90 minutes to ensure reasonable oxidation (and metal hydroxide precipitation) level for compounds like nitrites to nitrate which are usually oxidized at acidic to neutral range. The end pH correction was then carried out by adding NaOH until the pH was between the ranges of 6.9 before filtration was done.

D. Adsorption Studies

The effect of Nitrate adsorption was studied by measuring 300gm of the carbon materials into four different reaction columns (CPC and CPAC at the three activation levels). 1.5 litres of the oxidized wastewater was then added and 50ml filtrates drawn after reaction times of 2, 4, 6 and 8 hours.

1) Nitrate Measurement

The treated wastewater was first subjected to centrifuging at the speed of 4200 revolutions per minute for about 6 minutes the clear supernatant obtained was separated and used for the test. The Nitrate content of the wastewater was measured by adding HACH Nitra Ver®5 Nitrate pill in 25ml of the obtained supernatant; this was then vigorously mixed to ensure reaction. The compound was then left for about 7mins

to settle. A spectrometer (Spectrumlab 23A) was set to operate at a wavelength of 890nm with blanks used for calibration and quality check. The amount of nitrate adsorbed in mg/g at time t , (q_t) was computed using (3);

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (3)$$

where C_0 and C_t = nitrate concentrations at initial stage and after contact time t ; W = weight of carbon material (CPC & CPAC) in grams; V = the volume of filtrate drawn

The removal efficiency of the CPC and CPAC was calculated using the mathematical relation given by (4);

$$\text{Nitrate removal efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (4)$$

E. Adsorption Isotherm

The efficiency of the activated carbon in removal of nitrates from the wastewater was measured using adsorption isotherms. According to [24] adsorption isotherms are one of the useful experimental tools for describing how the adsorbate molecules distribute between the liquid and solid phase when adsorption process reaches an equilibrium state. For the purpose of this study, the Langmuir and Freundlich Isotherms were used to assess the adsorption in the treatment. The choice of isotherms is based on the assumptions on which they are based.

1) Langmuir Isotherm

In the Langmuir theory, the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent. For liquids (*adsorbate*) adsorbed on solids (*adsorbent*), the Langmuir isotherm can be expressed in linearized form by

$$\frac{C_e}{q_e} = \frac{1}{bQ^0} + \frac{C_e}{Q^0} \quad (5)$$

where C_e is the equilibrium concentration of adsorbate, q_e is the amount of the adsorbate at equilibrium, Q^0 and b are Langmuir's constants related to the capacity and energy of adsorption respectively. The graph of C_e/q_e versus C_e suggests the applicability or otherwise of the isotherm (straight line implies favourable).

2) Freundlich Isotherm

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface if the adsorbent. The Freundlich isotherm is expressed in the form as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (6)$$

where q_e is the amount of adsorbate adsorbed (mg/g), C_e is the residual concentration of adsorbate (mg/l), K_f is a constant which is a measure of adsorption capacity and $1/n$ is a measure of adsorption intensity. The Freundlich constants are determined by plotting the graph of $\log q_e$ against C_e . Although the Freundlich isotherm is widely used, it provides

no information on the monolayer adsorption capacity of the carbon material in contrast to Langmuir model [25].

III. RESULTS AND DISCUSSION

A. Characterization of Cassava Peel Activated Carbon at Different Activation Ratios

The result of characterization studies of CPC and CPAC at the various activation ratios shows a slight increase in bulk density. Table I shows that the ash content of the CPC at 0% activation ratio was slightly higher than the Zinc Chloride activated CPAC. This implies that the activated carbon had an overall higher level of carbon material yield.

TABLE I
CHARACTERISTICS OF CASSAVA PEEL ACTIVATED CARBON AT DIFFERENT ACTIVATION RATIO

ZnCl ₂ Impregnation Ratio	Ash Content (%)	Moisture content (%)	Bulk Density (%)
0:1	2.65±0.12	2.31±0.02	0.407±0.02
1:3	2.38±0.03	2.21±0.01	0.410±0.03
2:3	2.44±0.11	2.33±0.13	0.413±1.13
1:1	2.47±0.02	2.22±0.05	0.415±0.01

B. Pore Size Distribution

According to the definition by IUPAC, adsorbent pores are classified into three groups: micropores (diameter <2 nm), mesopores (2–50 nm) and macropores (>50 nm). The average pore length, average pore width average pore area and surface area of the CPAC were measured from the SEM images with the aid of Image J (Java interactive software). The results as displayed in Table II show that the CPC and CPAC had a predominant nature of mesopores, this shows that the carbon material should have good adsorptive characteristics.

C. Adsorption Isotherm Studies

1) Langmuir

Results from the Langmuir plots (Figs. 2-6) for the four activation levels shows that they all had coefficient values (R^2) between 0.999 and 0.5, this shows that the material followed the Langmuir theory assumptions i.e. the carbon surface was adsorbing on a site-specific, monolayer basis, this implies that the carbon material both in natural and activated state are effective adsorbents.

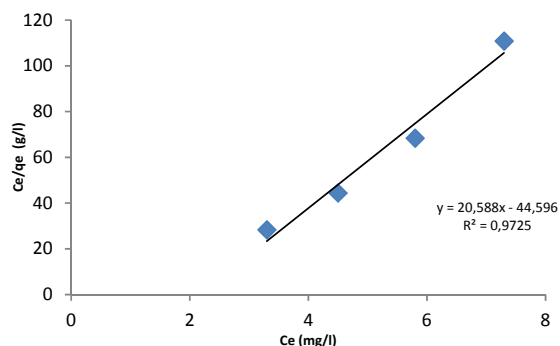
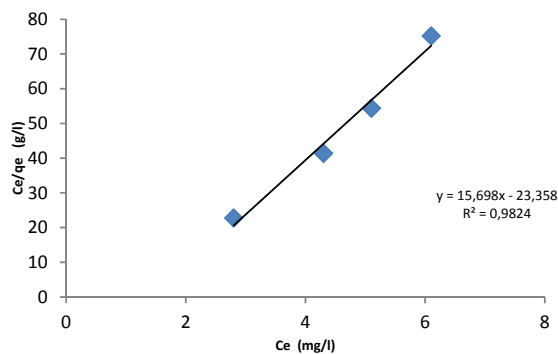
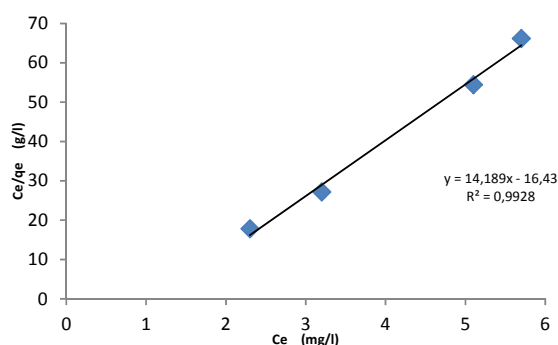
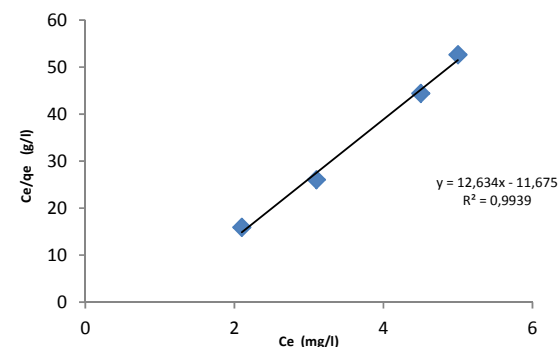
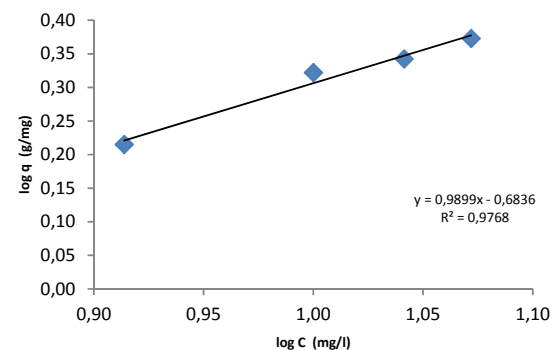


Fig. 3 Langmuir Isotherm for NO_3^- sorption at 0:1 activation ratio

Fig. 4 Langmuir Isotherm for NO³⁻ sorption at 1:3 activation ratioFig. 5 Langmuir Isotherm for NO³⁻ sorption at 2:3 activation ratioFig. 6 Langmuir Isotherm for NO³⁻ sorption at 1:1 activation ratioFig. 7 Freundlich Isotherm for NO³⁻ sorption at 0:1 activation ratioTABLE II
ANALYSIS OF PORE SPACE AND SURFACE AREA OF CASSAVA PEEL CARBON

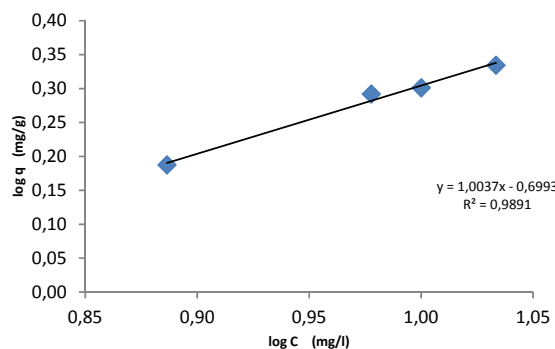
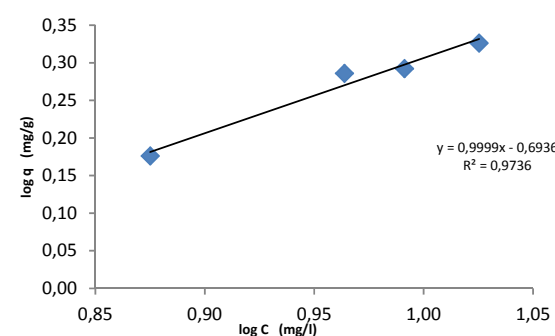
Sample	Average Pore Length (nm)	Average Pore Width (nm)
CPC (0:1)	13.8±0.2	10.4±0.2
CPAC (1:3)	25.2±0.1	16.7±0.1
CPAC (2:3)	27.7±0.1	18.9±0.1
CPAC (1:1)	37.3±0.2	28.7±0.2

Results were obtained from subjecting 1.5g of Cassava Peel Activated Carbon (CPAC) to SEM at Sheda Science and Technology complex, Sheda, Abuja, Nigeria.

The essential characteristics of the Langmuir isotherm can also be expressed using a dimensionless separation parameter denoted by R_α which indicates that the isotherm could be unfavorable ($R_\alpha > 1$), favorable ($0 < R_\alpha < 1$), linear ($R_\alpha = 1$) or irreversible ($R_\alpha = 0$). R_α defined by,

$$R_\alpha = \frac{1}{1 + bC_0} \quad (7)$$

where b is the Langmuir constant and C_0 is the initial concentration of adsorbate. R_α values for the Langmuir analysis of the four levels of ZnCl₂ activation showed that they all fell within the range ($0 < R_\alpha < 1$), with values of 0.15, 0.11, 0.09 and 0.07 for the 0:1, 1:3, 2:3 and 1:1 activation levels respectively.

Fig. 8 Freundlich Isotherm for NO³⁻ sorption at 1:3 activation ratioFig. 9 Freundlich Isotherm for NO³⁻ sorption at 2:3 activation ratio

2) Freundlich

Under the Freundlich adsorption theory the K_f and n denotes the adsorption capacity and adsorption intensity respectively, these values were determined from the intercept and slope of the plots (Figs. 7-10). A value of $n^{-1} > 1$ was

obtained from the four carbon materials (0:1, 1:3, 2:3 and 1:1 activation levels) indicates a favorable adsorption of nitrate on the CPC and CPAC this is also in agreement with findings of [26].

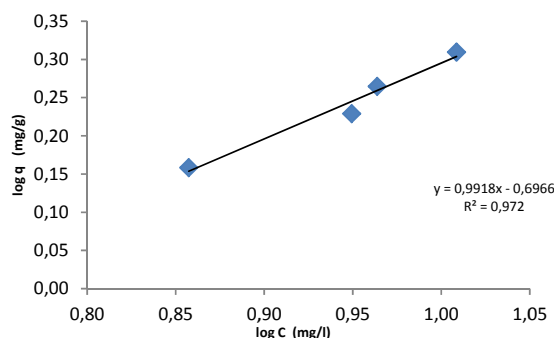


Fig. 10 Freundlich Isotherm for NO_3^- sorption at 1:1 activation ratio

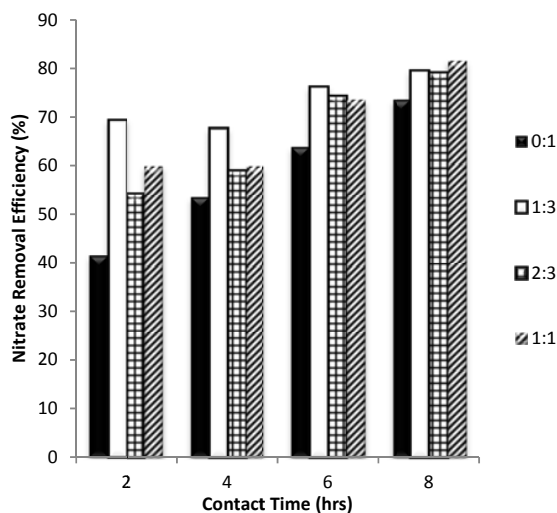


Fig. 11 Comparison of Nitrate removal efficiencies of CPC and CPAC after 2,4,6 and 8 hours contact time

D. Nitrate Removal Efficiency

Results obtained at the end of the treatment process shows that the cassava peel carbon and cassava peel activated carbon was able to effectively reduce the nitrate level in the wastewater. A close observation of the plot of nitrate decontamination level versus ZnCl_2 activation levels (Fig. 11) shows that the CPC could only effect a decontamination rate of 40% after 2 hours contact time, however the decontamination rose progressively to about 70% nitrate decontamination level after the 8 hour treatment period. The CPAC the 1:0 exhibited the highest decontamination level after 2 hours of 69.5% which also rose steadily to a total efficiency of 73.6% after 8 hours contact time. The CPAC at 1:1 activation level had an initial decontamination level of 60% after the 2 hour period and the highest decontamination level of 81.6% after the 8 hour period. This result shows that CPAC at 0:1 would be effective in situations where there is need to rapidly remove nitrate from solution within a short

period while the 2:3 and 1:1 CPAC would be more effective for long term nitrate removal.

IV. CONCLUSION

From this study it can be concluded that the carbon as well as the activated material produced from cassava peels is effective in adsorption of nitrates. The carbon material however had some very important characteristics which are worthy of note. This includes the fact that ordinary carbon produced from cassava peels had very high adsorption characteristics (about 73.6% decontamination after 8 hours); however, when activated the CPAC at 1:3 showed a very rapid decontamination rate (starting at about 69.5% after 2 hours). Although the 1:1 showed a slower rate of decontamination when compared to CPAC at 1:3, the latter had a higher decontamination rate after 8hrs contact time this shows that these two categories of activated carbons could be utilized for two different removal intensities. The use of this carbon material could serve as a method of treatment of nitrogen related environmental problems such as eutrophication and algae blooms if utilized in appropriate quantities.

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