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Nitrate and Phosphate Adsorption Studies in Cassava Processing Wastewater using Activated Carbon Derived from Cassava Peels

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Abstract

Nitrate and Phosphate contamination of water play a major role in the proliferation of eutrophic lakes and algae blooms in water bodies. These are major environmental issues as far as water bodies are concerned. Cassava Peel Carbon (CPC) was produced by carbonising cassava peels which were then chemically activated using Zinc chloride ($ZnCl_2$) at two different activation ratios (2:3 and 1:1) to obtain Cassava Peel Activated Carbon (CPAC). Results from the studies showed that CPAC at both activation levels had slightly higher affinity for nitrate as opposed to phosphorus ions in cassava processing wastewater. A comparison of the decontamination levels of nitrate and phosphate ions in the wastewater by CPAC at 2:3 and 1:1 $ZnCl_2$ activation levels show that both activated carbon materials were able to achieve of decontamination level of over 80 and 70% of the initial nitrate and phosphate ion concentrations respectively. Findings suggest that this adsorbent could be a treatment option for eutrophic water bodies if applied with appropriate dosage.

Keywords: Activated carbon; Adsorption; Cassava peels; Nitrate; Phosphate

Introduction

Water is a resource that is unique to the earth and also crucial to the existence of life on it. According to Fakayode (2005), water represents the most abused, poorly managed and polluted resource by man. Access to clean water is gradually dwindling due to continuous pollution of existing water bodies. With increasing global population, the gap between the supply and demand for water is not only widening, but has reached alarming levels now is posing a threat to human existence in some locations. Yingchun *et al.* (2013) observed frequent occurrence of water crises on a global scale due to climate change and the increased intensity of human activity.

Nitrates result in severe environmental problems like eutrophication and algae boom. Nitrate has also been identified as the cause of mortality due to disease infections, such as cyanosis and cancer of the alimentary canal (Wang *et al.,* 2007) and blue baby syndrome (methemoglobinemia) in infants (Ako *et al.,* 2014). Pollution resulting from agricultural activities can cause a significant deterioration of surface and groundwater quality. Demiral and Gunduzoglu (2011) observed that various types of agricultural, domestic and industrial wastewater contain several nitrogenous compounds such as ammonia, nitrates and nitrites and are frequently noticed in water bodies.

Phosphates on the other hand are considered as the growth limiting nutrient for plants and microbial growth (Muñoz *et al.* (1997). They are responsible for controlling freshwater and terrestrial ecosystems productivity (Zhang *et al.,* 1998). The uses of phosphate include manufacture of cleaning products, toothpaste, fire extinguishers, textile processing and food (Weiner *et al.,* 2001). Phosphate also contributes to eutrophication in water bodies when its presence is in excess.

Adsorption through the use of activated carbon is one of the scientifically accepted methods of purification and treatment of gasses (Vargas *et al.,* 2012) and industrial effluents (Omotosho and Sangodoyin 2013). Foo and Lee 2010) also confirmed Activated Carbon (AC) as one of the most popular adsorbents used in industries for the removal and recovery of organic and inorganic compounds from gaseous and liquid streams.

This study aims at comparing Nitrate and Phosphate adsorption from cassava processing wastewater using activated carbon derived from cassava peels.

Materials and Methods

Cassava peel activated carbon production

The CPAC was produced by collecting cassava (*Manihot esculenta Crantz*) peels from a cassava processing industry in Ibadan, Nigeria. The cassava peels were physically inspected, washed and sundried to a moisture content of between 8 and 10% wet basis (Plate 1).

Plate 1: Inspected, washed and sun dried Cassava peels

The dried cassava peels were then carbonized in a muffle furnace (Carbolite, England Model AAF 11/18) at a temperature of 420 °C for a period of 90 mins. The resulting carbon material was allowed to gradually cool down overnight in the furnace under inert conditions. The resulting carbon material (Plate 2) was reduced to a size range of 450-500µm by pounding in a mortar and sieving firstly through a 500µm sieve and then a 450µm sieve. The carbon material left on the sieve was then collected. The reduced carbon was pre-washed to remove any form of dirt that may have adhered to it during the size reduction process. It was later dried an oven at 120^{0}C for 8 hrs.

Two 300gm samples of the obtained Cassava Peel Carbon was weighed using a digital precision weighing balance (AND GF-2000) and then activated using $ZnCl_2$ at activation ratios of 2:3 and 1:1 (activating agent : carbon material) as described by Omotosho and Sangodoyin (2013). These two activation levels were selected because they offered comparable carbon quality characteristics.

Plate 2: Carbonized cassava peels

Characterisation of cassava peel activated carbon

1.5grams of each of the CPC and CPAC was subjected to test in a Scanning Electron Microscope (ZEISS EVO® MA 15) to reveal some physical microscopic characteristics such as pore development and distribution. The image obtained was then analysed with the aid of Image J (a Java Interactive Software) to give a more pictorial 3-dimesional view of the surface of the carbon material. The average pore size was also determined with the aid of the SEM image and a software programme.

Wastewater collection and pre-treatment

Wastewater sample (25 L) was collected from the same cassava processing industry where the peels were obtained. The sample was collected in opaque plastic materials and kept under ice to reduce deterioration and change in composition due to light and temperature during the process of transportation to the laboratory. The wastewater was taken to alkaline range by adding of 0.5 M NaOH until a pH of 10.0 was attained. Hydrogen peroxide at 50% concentration was then added at a dose of 0.5 grams H_2O_2 per gram of CN^- content. Wastewater was left for 2 hrs to ensure a reasonable level of oxidation and cyanide destruction before filtration was done in an intermediate sand filter column constructed from transparent Perspex of dimensions 4 mm thickness, 0.15 m length, 0.15 m breath and 1.4 m height.

Adsorption isotherms studies

Specially constructed transparent Perspex adsorption columns of 3mm thickness, 0.1 m length, 0.1 m breath and 0.65 m height were filled with the CPC and CPAC at activation levels 2:3 and 1:1. The filtered wastewater was released simultaneously into the adsorption columns at the rate of 0.378 L/hr. Water samples were strained from the three adsorption columns after a period of 2, 4, 6 and 8 hrs as recommended by Ijaola (2011). Results from these effluent obtained from the treatments were then used in the adsorption studies using adsorption isotherms. According to Hameed et al. (2006) adsorption isotherms are useful experimental tools for describing how the adsorbate molecules distribute between the liquid and solid phase when adsorption process reaches an equilibrium state. In this study, the Langmuir Isotherm was used based on the assumption 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 as

$$\frac{C_e}{q_e} = \frac{1}{bQ^0} + \frac{C_e}{Q^0} \quad (3)$$

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 (near straight line) or otherwise (considerable degree of scatter) of the isotherms.

According to Dada *et al.,* (2012), the essential separation characteristics of the Langmuir isotherm (R) can also be expressed using a dimensionless parameter which indicates that the isotherm could be either unfavorable (R>1), favorable (0<R<1), linear (R =1) or irreversible (R=0). R_{is} defined by the expression,

$$R_{\propto} = \frac{1}{1 + bC_0} \quad (4)$$

Where

b is the Langmuir constant

C_0 is the initial concentration of adsorbate.

Nitrate and phosphate concentration measurement

The treated wastewater was first subjected to centrifuging at a speed of 4200 rpm for about 6 min. The clear supernatant was separated and used for the test. Nitrate content of the wastewater was measured using the Colorimetric, Brucine method with the aid of Spectrophotometer (Spectrumlab 23A) which was set to operate at wavelength of 410 nm with blanks used for calibration and quality check.

The Phosphate content was tested by adding one sachet of HACH PhosVer®3 reagent powder to 10 ml of the obtained supernatant and also vigorously mixed and allowed to rest for 7 mins then subjected to spectrophotometry at a wavelength of 213.6 nm with blanks also used for calibration and quality check. Concentration in mg/l of Nitrate and Phosphate was obtained at the beginning and end of the adsorption process. The amount of nitrate and phosphate adsorbed in mg/g at time t was computed using equation (1) as recommended by Oghenejobh et al., (2008).

$$Amount\ of\ Nitrate/Posphate\ adsorbed = \frac{(C_0 - C_t)V}{W} \quad (1)$$

Where:

C_0 and C_t are nitrate/phosphate concentrations at initial stage and after contact time t in mg/l

W is weight of carbon material (CPAC) in grams

V is the volume of filtrate drawn in litres

Nitrate and phosphate removal efficiency

The removal efficiency of the Nitrate and Phosphate was calculated as follows:

$$Removal\ efficiency\ (\%) = \frac{C_0 - C_t}{C_0} X\ 100 \quad (2)$$

Where

C_o is the initial concentration in mg/l

C_t is the concentration after time t in mg/l

Result and Discussion
Characteristics of adsorbents

The physical characteristics of the carbon materials used as adsorbent in the study shows that the CPAC at 1:1 activation ratio had a slightly higher ash content than CPAC at 2:3 activation ratio although the value was lower than that of the CPC. This shows that the carbon material became more thermally stable with increase in activation ratio. The bulk density of the CPAC increased as the activation ratio increased. However the moisture content followed a reverse trend (Table 1).

Pore size distribution

According to IUPAC, adsorbent pores are classified into three groups: micropores (diameter <2 nm), mesopores (2–50 nm) and macropores (>50 nm). The results for the ash content of the three carbon materials were within the prescribed region of less than 8 % as recommended by Gin *et al.,* (2014) the values for moisture content and bulk density were also within recommended range of 2-8% and 0.4-0.5% respectively. 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 shown in Table 2 reveals that the CPC and CPAC had a predominant nature of mesopores, this shows that the carbon material has good adsorptive characteris-

Table 1: Characteristics of CPC and CPAC at different Activation ratio

Sample	Ash Content (%)	Moisture content (%)	Bulk Density (%)
CPC (0:1)	2.65±0.12	2.35±0.17	0.407±0.013
CPAC (2:3)	2.44±0.11	2.33±0.13	0.413±0.113
CPAC (1:1)	2.47±0.02	2.22±0.05	0.415±0.014

Table 2: 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±0.1	10.4±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.

Pore Development

Samples of the CPAC examined with the aid of a Scanning Electron Microscope show that the 2:3 activation ratio had a shallow pore development with honeycomb/hexagonal structure as shown in Plate 3. The Image J plot (figure 1) shows that the carbon had a rough surface structure which is indicative of a larger surface area/unit area of carbon material. The CPAC at 1:1 activation ratio on the other hand had a spongy and much deeper pore development (Plate 4). The Image J surface plot shown in figure 2 also confirms a more pronounced roughness in its surface physical structure. These exhibited features conform to good adsorption characteristics of the adsorbent materials.

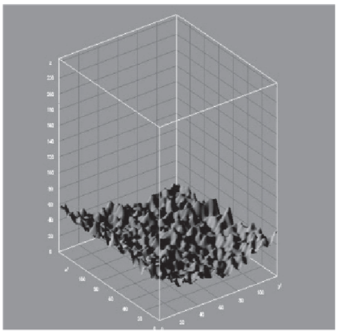

Figure 1: Surface plot of CPC at 0:1 activation ratio

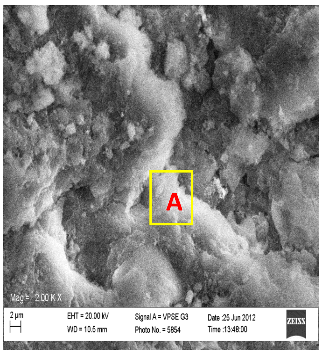

Plate 2: CPC at 0:1 activation ratio

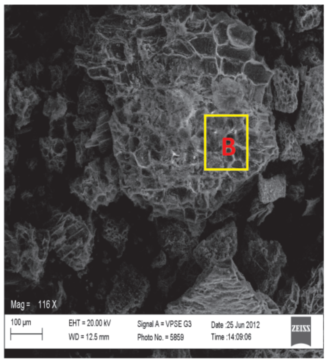

Plate 3: CPAC at 2:3 activation ratio

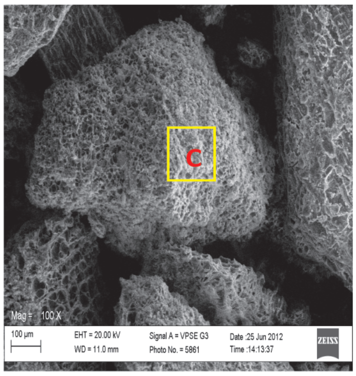

Plate 4: CPAC at 1:1 activation ratio

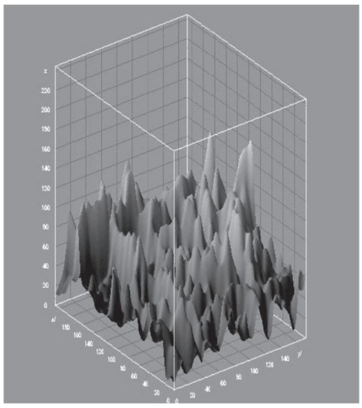

Figure 5: Surface plot of CPAC at 2:3 activation ratio

Langmuir Isotherm Results

Figures 4-7 show the Langmuir adsorption isotherms for nitrate and phosphates at 2:3 and 1:1 Zinc chloride activation. The result for all four isotherms show that they are all First-Order adsorption relationships. The Isotherms also reveal that the R^2 value for phosphate adsorption for 1:1 adsorption was 0.9974 while that for 2:3 was 0.9934. These values were more closer to 1 than those of nitrates which were 0.9725 for 1:1 and 0.9824 for 2:3 although both values were very close to and lie in the range 0 R 1 which is defined as being 'Favourable' and well fitted to the Langmuir isotherm model . These values according to Dizadji *et al.,* (2011) as well as Metacaf and Eddy (2003) also indicate chemosorption mechanism involvement in the sorption. It can also still be infered from the results that the phosphate adsorption by the carbon material was was better fitted to the Langmuir isotherm model than nitrate adsorption. In conclusion the both nitrate and phosphate ion adsorption patterns could be viewed as being adequately fitted to the Langmuir isotherm i.e. the carbon surface adsorbs at specific homogenous sites within the activated carbon material.

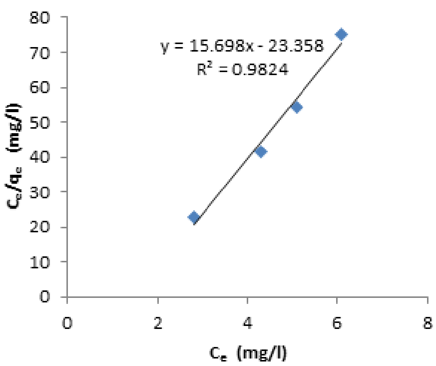

Figure 4: Langmuir Isotherm for NO_3^- sorption at 2:3 activation ratio

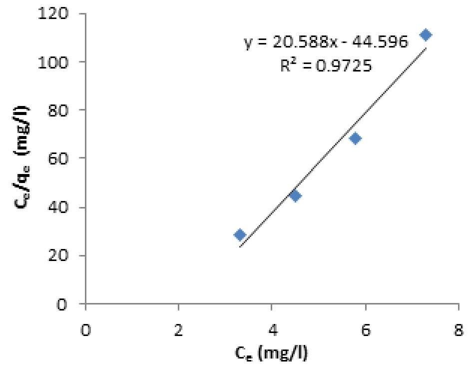

Figure 5: Langmuir Isotherm for NO_3^- sorption at 1:1 activation ratio

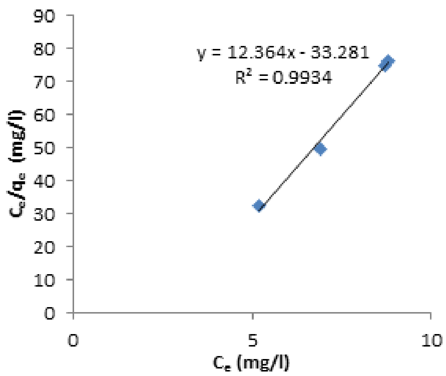

Figure 6: Langmuir Isotherm for PO_4^{3-} sorption at 2:3 activation ratio

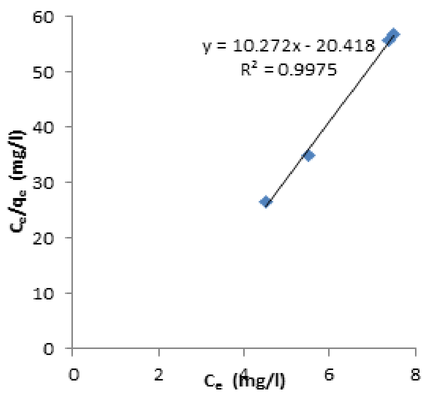

Figure 7: Langmuir Isotherm for PO_4^{3-} sorption at 1:1 activation ratio

Langmuir isotherm separation characteristics (R)

A critical assessment of the Langmuir isotherm value, R for the CPC and the two levels of $ZnCl_2$ activation as shown in Table 3 indicates that they fell within the range $0<R<1$ for both Nitrate and Phosphate ion adsorption from cassava processing wastewater indicating a favorable adsorption characteristics.

Table 3: Comparison of CPC and CPAC Langmuir R_α values for Nitrate and Phosphate Adsorption

Activation ratio	R_α Values	
	NO_3^-	PO_4^{3-}
0:1	0.15	0.23
2:3	0.09	0.13
1:1	0.07	0.10

The result also shows that the Langmuir R reduced with increase in activation levels for both phosphate and nitrate which indicates decreasing favorability of adsorption nature of the material with increase in activation level confirmed by Dada *et al.,* (2012).

A comparison of the decontamination levels of the two levels of activation of the CPAC for nitrate and phosphate ions in wastewater (Table 4) shows that at the nitrate decontamination level at 1:1 activation was constant at 60% over the first 4 hours, it however increased and eventually the highest for both the phosphate and nitrate contents. After 8 hours results obtained were above 70 % at both activation levels for nitrate and phosphate content. The general trend reveals that the decontamination level for nitrate and phosphate ions increased with contact time. Conclusively it can be concluded that the carbon material had more affinity for nitrate at both levels of activation. This shows that CPAC can be utilised in adsorption and control of nitrates and phosphates in water treatment process.

Table 4: Nitrate and Phosphate Decontamination Efficiency of CPAC at 2:3 and 1:1 Zn_2Cl Activation Ratio (%)

Contact Time (hrs)	NO_3^{-**} Activation ratio		PO_4^{3-**} Activation ratio	
	2:3	1:1	2:3	1:1
2	54.4	60.0	50.8	58.1
4	59.2	60.0	51.4	58.7
6	74.4	73.6	61.5	69.3
8	79.2	81.6	71.0	74.9

NB: Initial concentration of Nitrate= 10.6 mg/L, while that of Phosphate= 14.8 mg/L,
** values are in percentage

Conclusion

A laboratory scale study of cassava peel activated carbon as adsorbent for Nitrate and Phosphate removal in cassava processing water shows promising results. The Langmuir adsorption isotherm fitted the data. This adsorbent could be used for lowering Nitrate and Phosphate levels in eutrophic water bodies if applied in appropriate dosage. The CPAC has a slightly higher affinity for nitrates than phosphate ions in wastewater.

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